3a*H*-Indenes. Part 2.[1] Cycloaddition Reactions of 3-Methoxy- and 3-Trimethylsiloxy-3a-methyl-3a*H*-indene

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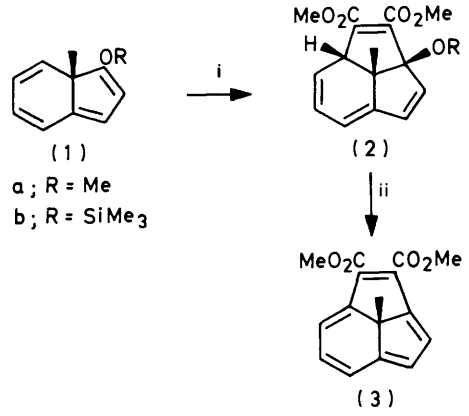
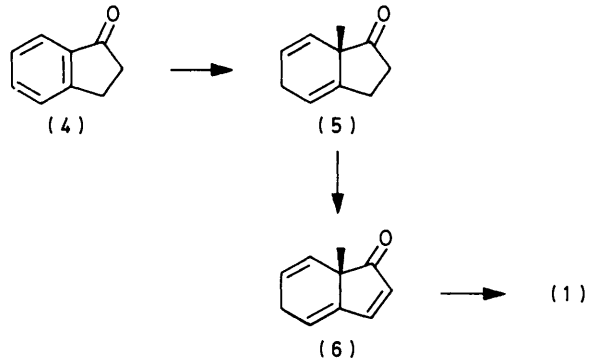
The title 3a-methyl-3a*H*-indenes (1a) and (1b) have been prepared from indan-1-one *via* the dienone (5) and the trienone (6), and the preparation of the key intermediates (5) and (6) has been improved. The 3a*H*-indene (1b) behaves similarly to the methoxy derivative (1a), and rearranges on heating to the 1*H*-isomer. Cycloaddition reactions of (1a) to *N*-phenylmaleimide and maleic anhydride give isolable [4 + 2]-adducts (12), which rearrange on heating to give the *exo*- and *endo*-[8 + 2]-adducts (13) and (14). In contrast, both 2-chloroacrylonitrile and 2-chloroacryloyl chloride give [8 + 2]-adducts with (1a). The 2-chloroacryloyl chloride adducts are readily converted into the tricyclic ketone (23). The trimethylsiloxy 3a*H*-indene (1b) undergoes cycloaddition reactions with dimethyl acetylenedicarboxylate, 2-chloroacryloyl chloride, and dichloroketene. The trimethylsilyl derivative (1b) offers some advantages over the methoxyindene (1a) in synthetic work.

We have recently reported the first preparation of an isolable simple 3a*H*-indene derivative (1a).[1] 3a*H*-Indenes are of interest since MNDO molecular orbital calculations suggest that they are the least stable of all the isomers of indene,[2] and because they readily participate in both [4 + 2] and [8 + 2] cycloaddition reactions.[1] Indeed the cycloadducts themselves are of interest since it has been shown that the formal [8 + 2] cycloadduct (2a) of (1a) with dimethyl acetylenedicarboxylate (DMAD) is easily converted into the tricyclic [10]annulene (3), a new aromatic system (Scheme 1).[3]

We have now investigated the cycloaddition reactions of both (1a) and the closely related trimethylsiloxy derivative (1b) with other 2π-components. The overall route to these 3a*H*-indene derivatives remains the same, and is based on the reductive alkylation of indan-1-one (4), followed by introduction of an extra double bond, and ' extended ' enolisation (Scheme 2). However, we have made significant improvements which allow these steps [(4) ⟶ (5) ⟶ (6)] to be carried out in higher yield and on a much larger scale.



Scheme 1. *Reagents:* i, $MeO_2CC{\equiv}CCO_2Me$; ii, H^+



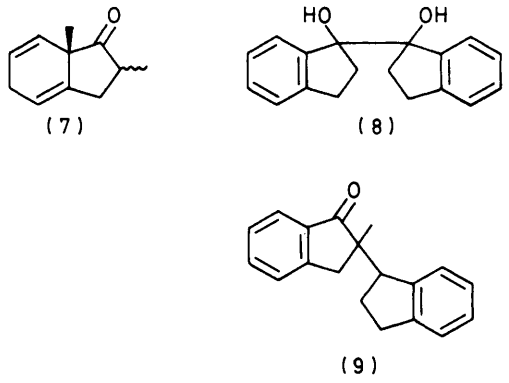
Scheme 2.

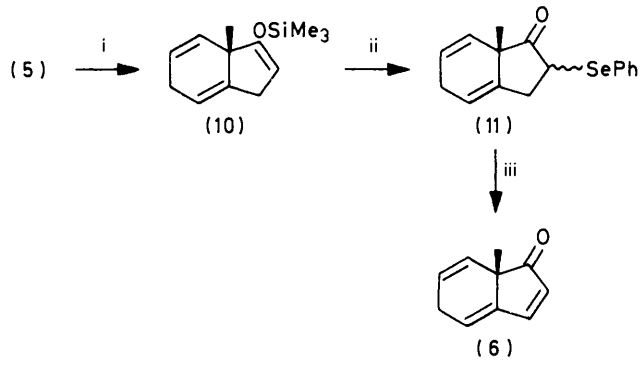
Results and Discussion

Reductive Alkylation of Indan-1-one [(4) ⟶ (5)].—The dissolving metal reduction of indan-1-one has been studied previously.[1,4] Potassium metal was added to a solution of (4) in liquid ammonia containing t-butyl alcohol and tetrahydrofuran (THF), and the reaction was quenched with iodomethane as previously described.[1] However, in our hands, these reaction conditions gave rise to many products, and the required dienone (5) was isolated in only 18% yield. The by-products, which were separated by chromatography, were identified as the over-methylated dienone (7) (6%), 2,2-dimethylindanone (9%), 2-methylindanone (3%), indan-1-ol (7%), 1,1'-dihydroxybi-indan-1-yl (8) (2.5%) and 2-indan-1-yl-2-methylindan-1-one (9) (5%). The formation of 2,2-dimethylindanone was particularly undesirable since it could not be completely separated from the required dienone (5) either by chromatography or by distillation.

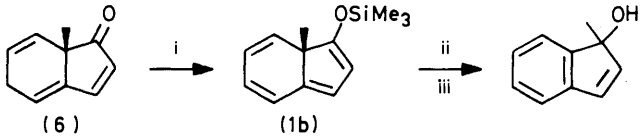
These unwanted by-products are a result of coupling reactions favoured by the presence of excess of indan-1-one in the reaction mixture, and over-methylation caused by the excess of iodomethane. In order to avoid these problems the order of addition of reagents was altered, and the amount of iodomethane was reduced to just over one equivalent. Thus indan-1-one in THF containing t-butyl alcohol was added to a preformed solution of potassium in liquid ammonia. Under these conditions, the yield of the required dienone was routinely >50%. When the reaction was carried out on a large scale using 118 g of indan-1-one, distillation of the crude product through an efficient fractionating column gave the dienone (5) (53%) that was sufficiently pure for the next stage.

Conversion of the Dienone (5) *into the Trienone* (6).—The introduction of the necessary extra unsaturation had already proved difficult.[1] The best procedure involved α-phenylselenation of the lithium enolate of compound (5) with phenylselenyl bromide, and oxidation of the selenide with





Scheme 3. *Reagents:* i, Me_3SiCl, NaI, Et_3N, MeCN, 40 °C; ii, PhSeBr, THF, −78 °C; iii, H_2O_2, H_2O, pyridine, THF, 5 °C



Scheme 4. *Reagents:* i, Me_3SiCl, NaI, Et_3N, MeCN, 35 °C; ii, C_6H_6, reflux; iii, KF, THF, H_2O, Bu^n_4NOH

hydrogen peroxide. Although in small scale reactions, satisfactory yields of the product (6) could often be obtained, on a larger scale the yield was routinely in the range 25—40%, and considerable amounts of the starting material (5) were always recovered. The problem was not in the oxidation step, alternative procedures involving the use of 3-chloroperbenzoic acid [5] or chloramine-T [6] giving no improvement, but in the initial selenation, n.m.r. analysis of the crude selenide showing it to be a mixture of several compounds. The major problem is thought to be further deprotonation of the selenide (11) by the enolate of (5), thereby accounting for both the returned (5), and subsequent by-product formation from (11). Neither the use of phenylselenyl chloride, nor inverse addition procedures made any significant improvement.

Therefore, in order to circumvent the problems caused by acid–base reactions involving the enolate of (5), the use of a preformed enol derivative was investigated (Scheme 3). The trimethylsilyl enol ether (10) was readily prepared from compound (5) by treatment with chlorotrimethylsilane and triethylamine in acetonitrile containing sodium iodide.[7] This method was found to be superior to silylation of the enolate anion. Reaction of the enol derivative (10) with phenylselenyl bromide in THF at −78 °C gave the required selenide (11). The selenide prepared in this way was virtually pure by n.m.r. Oxidation of (11) with hydrogen peroxide in the presence of pyridine [8] then gave the required trienone (6) in an acceptable overall yield, and by a method amenable to large scale work.

A by-product in the oxidation step is 2-methyl-(*E*)-cinnamic acid, which is probably formed by way of a competing Baeyer–Villiger oxidation of the selenide (11) or the selenoxide. This by-product was not formed by over-oxidation of the trienone (6), which was stable to the reaction conditions. Furthermore, if the cinnamic acid resulted from oxidation of (6) then it would be expected to have (*Z*)-geometry. In a related selenide oxidation, the formation of by-products was attributed to over-oxidation of the required enone.[6] However, our findings suggest that in these systems the competing Baeyer–Villiger oxidation probably occurs *before* selenoxide elimination.

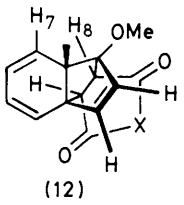
Generation of 3aH-*Indenes* (1) *from the Trienone* (6).—The fully conjugated 3-methoxy-3a*H*-indene derivative (1a) was prepared by deprotonation of the trienone (6) with potassium hydride in 1,2-dimethoxyethane (DME) in the presence of one equivalent of 18-crown-6, and quenching of the resulting enolate with methyl fluorosulphonate as previously described.[1]

The trimethylsiloxy derivative (1b) was conveniently prepared from (6) by treatment with chlorotrimethylsilane–sodium iodide–triethylamine [7] in acetonitrile at 35 °C, or by reaction with trimethylsilyl trifluoromethanesulphonate in ether in the presence of triethylamine.[9] The 3a*H*-indene (1b) is an unstable bright yellow oil. On being heated, it rearranges in a similar manner to the methoxy derivative (1a) to give a 1*H*-indene derivative which, on removal of the trimethylsilyl group, gave the known [10] 1-methyl-1*H*-inden-1-ol (Scheme 4). The use of the trimethylsilyl derivative (1b) has the advantage of avoiding the use of the highly toxic methyl fluorosulphonate.

Cycloaddition Reactions of the 3aH-*Indene* (1a).—The cycloadduct (2a) is readily converted into the annulene (3). However, the subsequent conversion of (3) into the parent unsubstituted annulene involves the use of the expensive tris(triphenylphosphine)rhodium(I) chloride.[3,11] This problem prompted an investigation into the use of other dienophiles to intercept the 3a*H*-indene (1a).

(*a*) *With* N-*phenylmaleimide and maleic anhydride.* Although the reaction of (1a) with *N*-phenylmaleimide has been reported already,[1] the detailed stereochemical assignments of the adducts were not discussed. Addition of *N*-phenylmaleimide to a solution of (1a) gave the *endo*-[4 + 2]-adduct (12a) (47%). The *endo* stereochemistry was established by nuclear Overhauser effect (n.O.e.) difference experiments. Thus pre-irradiation of the methoxy group gave strong enhancements of the signals due to 2- and 8-H, and lesser enhancements of 7-H and the ring junction methyl group. Pre-irradiation of 8-H caused enhancement of 7-H thereby confirming the *endo* stereochemistry.

Initial studies on the cycloaddition of maleic anhydride to compound (1a) resulted in mixtures of adducts in poor yield. However, by working up the reaction mixture below 0 °C, using an ice-water-jacketed chromatography column, and including some acetic anhydride in the column eluant to prevent hydrolysis of the adducts on the column, it has now been possible to isolate the *endo*-[4 + 2]-adduct (12b) as an unstable solid. Heating this adduct gave a 2 : 3 mixture of the *exo*- (13b) and *endo*- (14b) [8 + 2]-adducts. The half-life for the rearrangement of (12b) to (13b)/(14b) is *ca.* 10 min at 35 °C. The relative stereochemistry was assigned on the basis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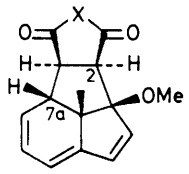
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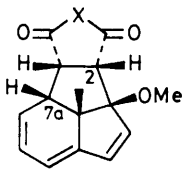
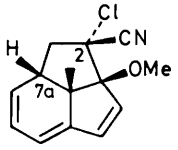

(14)

a; X = NPh
b; X = O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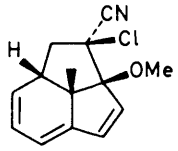
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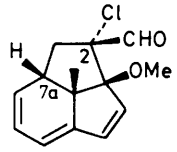
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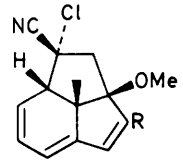
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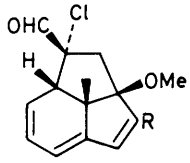
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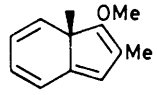
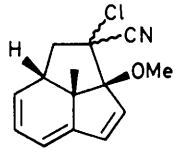
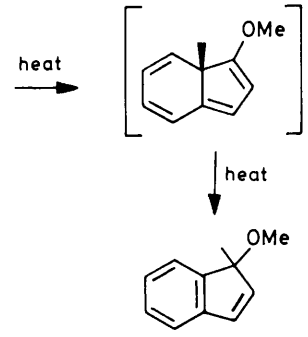

(20)

a; R = H
b; R = Me


(15) / (16)



Scheme 5.

of n.O.e. experiments. Pre-irradiation of the methoxy group gave an enhancement of the signal for 2-H only in the more polar *endo*-isomer (14b) in which 2-H and the methoxy group have a *cis*-relationship. Both isomers showed the expected strong enhancement of 7a-H when the central methyl group was pre-irradiated. The [4 + 2]-*N*-phenylmaleimide adduct (12a) also rearranges on heating to a mixture of [8 + 2]-adducts, (13a) and (14a), although a higher temperature is required. The stereochemical assignments of (13a) and (14a) follow by comparison of their n.m.r. spectra with those of compounds (13b) and (14b).

The non-interconvertibility of the [8 + 2]-adducts on heating was taken as evidence for a dissociation–recombination mechanism for the thermal rearrangement of the [4 + 2]-adducts.[1] Further support for this mechanism has been obtained. When the adduct (12b) is warmed in the presence of *N*-phenylmaleimide, the corresponding adduct (12a) can be isolated. The [8 + 2]-DMAD adduct (2a) is formed when (12a) or (12b) are heated in the presence of DMAD at 110 and 40 °C, respectively. These experiments confirm that the 3a*H*-indene (1a) is an intermediate in the rearrangement process. In a complementary experiment, the [4 + 2]-adduct (12b) was warmed in ether with cyclopentadiene. Here it is the maleic anhydride that is trapped, and a bright yellow solution of the 3a*H*-indene (1a) remained.

Attempts to effect oxidative bis-decarboxylation of the [8 + 2]-maleic anhydride adducts by electrochemical methods [12] were unsuccessful.

(*b*) *With 2-chloroacrylonitrile.* The commercially available dienophile, 2-chloroacrylonitrile, reacted with the 3a*H*-indene (1a), although the reaction mixture had to be heated to 60 °C to achieve the cycloaddition. Separation of the reaction products by column chromatography gave first a 55% yield of a mixture of the [8 + 2]-adducts (15) and (16) in a 3 : 1 ratio. When the mixture was cooled in ice, the major isomer (15) crystallised out. The structure of these adducts was assigned on the basis of the n.m.r. spectrum, which showed a pattern of olefinic resonances very similar to that of the other [8 + 2]-adducts already described. Coupling between 7a-H and the dienophile protons confirmed the regiochemistry of the cycloaddition. The relative stereochemistry at C-2 was established by n.O.e. measurements on the aldehyde (17), prepared by reduction of compound (15) with di-isobutylaluminium hydride. Thus an enhancement of the aldehyde proton was observed on pre-irradiation of either 7a-H, the methyl, or the methoxy protons.

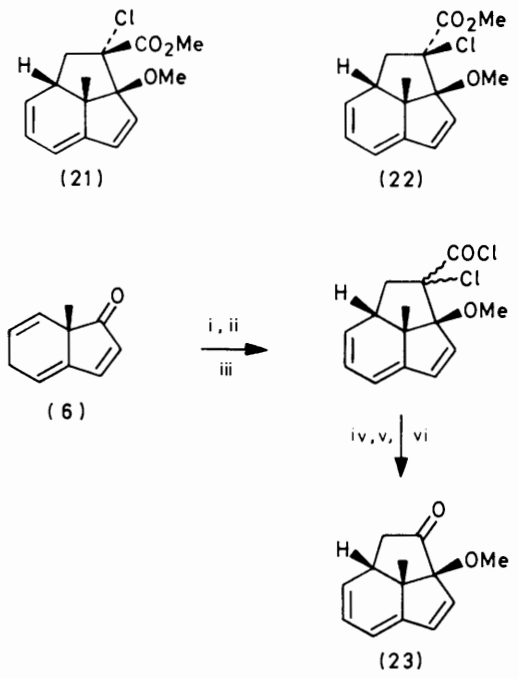
Further elution of the chromatography column gave a mixture of two further adducts (18a) and (18b). This mixture had an identical u.v. spectrum ($\lambda_{max.}$ 305 nm) with that of (15) indicating the same triene chromophore to be present, but in the n.m.r. spectrum the dienophile protons were not coupled to 7a-H indicating the alternative regiochemistry of the adducts. The stereochemistry was determined in a similar way to that of the adduct (15) by n.O.e. measurements on the derived mixture of aldehydes (19).

The formation of the homologue (18b) can be explained by cycloaddition to the over-methylated 3a*H*-indene (20). Since the starting trienone (6) was pure, the extra methyl group must have been introduced during the enolisation–methylation step, by initial *C*-methylation. The 3a*H*-indene (20) appears to react with 2-chloroacrylonitrile to give the adduct (18b) exclusively; no regio- or stereo-isomers were detected. This unusual regiospecificity is possibly due to steric repulsion between the extra methyl group and the bulky end of the dienophile, and to the hyperconjugative electron release of the extra methyl group.

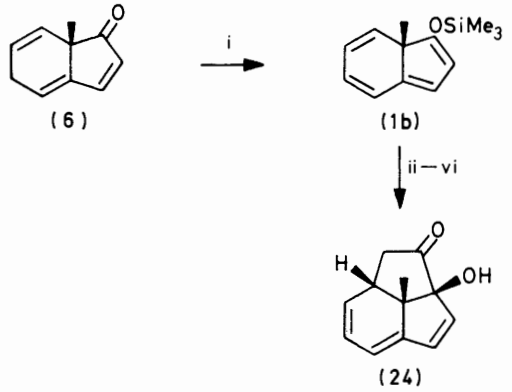
Under flash vacuum pyrolysis conditions a mixture of the adducts (15) and (16) underwent retro-[8 + 2]-cycloaddition to give 1-methoxy-1-methyl-1*H*-indene (Scheme 5).

2-Chloroacrylonitrile has found much use in recent years as a ketene equivalent, since hydrolysis of its cycloadducts gives ketones. However, the two sets of conditions commonly employed for this conversion, sodium sulphide in ethanol [13] or sodium hydroxide in ethanol and dimethyl sulphoxide,[14] failed to convert the adduct (15) into the corresponding ketone.

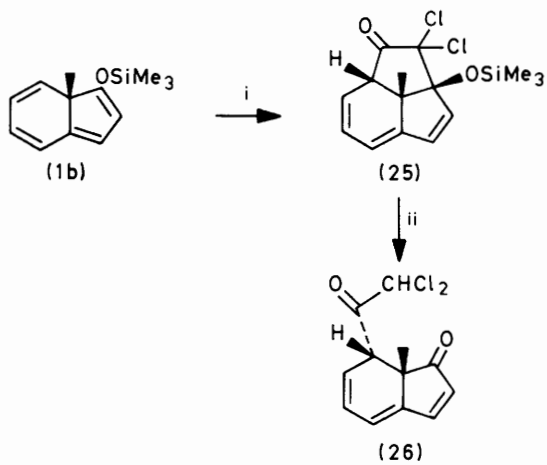
(*c*) *With 2-chloroacryloyl chloride.* Like 2-chloroacrylo-



Scheme 6. *Reagents:* i, KH, 18-crown-6, DME, −23 °C; ii, $MeOSO_2F$; iii, $H_2C{=}C(Cl)COCl$, −23 to 0 °C; iv, NaN_3, room temp.; v, reflux, DME; vi, AcOH, H_2O, 60 °C



Scheme 7. *Reagents:* i, $CF_3SO_2OSiMe_3$, DME, 0 °C; ii, $H_2C{=}C(Cl)COCl$; iii, NaN_3; iv, reflux, DME; v, AcOH, H_2O, 60 °C; vi, KF



Scheme 8. *Reagents:* i, $CHCl_2COCl$, Et_3N, Et_2O, reflux; ii, chromatography on silica gel

nitrile, 2-chloroacryloyl chloride is reported to be a useful ketene equivalent.[15] Although it is not commercially available it is easily prepared from methyl acrylate.[16] When 2-chloroacryloyl chloride was added to a solution of compound (1a) the colour of the indene was discharged by the time the reaction mixture had warmed up to 0 °C, in contrast to 2-chloroacrylonitrile which only reacted rapidly at 60 °C. No attempt was made to isolate the initial acid chloride adducts. Instead the mixture was treated with methanol and triethylamine to give, after work-up, the adduct (21) containing 1 part in 25 of the stereoisomer (22). None of the regioisomer was formed in contrast to the reaction of the less reactive 2-chloroacrylonitrile which gave both regioisomers and was less stereoselective. The esters (21) and (22) were also formed by heating the [4 + 2]-adducts (12a) or (12b) with 2-chloroacryloyl chloride, followed by treatment with methanol, although in these reactions a greater proportion of the stereoisomer (22) was formed. This is presumably related to the higher temperature of these reactions. Reduction of (21) with di-isobutylaluminium hydride gave an alcohol which on oxidation with chromium trioxide in pyridine gave the aldehyde (17), identical with the specimen prepared by reduction of (15), thereby confirming the stereochemistry of the adduct (21).

The conversion of the initial 2-chloroacryloyl chloride adducts into the ketone (23) was achieved by the standard procedure.[15] Thus treatment of the crude reaction mixture after the cycloaddition with sodium azide in DME followed by heating to 80 °C to effect the Curtius rearrangement, and finally acid hydrolysis, gave the tricyclic ketone (23) [48% from (6)]. The ketone (23) is a colourless oil with a carbonyl absorption at 1 732 cm^{-1}, and is of considerable value as a precursor to tricyclic [10]annulenes.[17,18] The route to this important tricyclic intermediate is summarised in Scheme 6.

Cycloaddition Reactions of the 3a*H*-*Indene* (1b).—(*a*) *With dimethyl acetylenedicarboxylate.* The trimethylsiloxy 3a*H*-indene (1b), generated from the indenone (6) by treatment with trimethylsilyl trifluoromethanesulphonate, reacted readily with DMAD to give, after acid work-up, the annulene diester (3) in good overall yield [54% from (6)]. No attempt was made to isolate the initial adduct (2b). The annulene diester prepared in this way solidified to give a yellow solid, m.p. 49—50 °C. When this ester (3) was prepared from the methoxyindene (1a), it was never obtained sufficiently pure to allow crystallisation. This represents another advantage of using the trimethylsiloxy derivative since it avoids the possible introduction of impurities during the enolisation–methylation sequence.

(*b*) *With 2-chloroacryloyl chloride.* The 3a*H*-indene (1b) reacted with 2-chloroacryloyl chloride to give an adduct which was treated as before to give the tricyclic ketone (24), hydrolysis of the trimethylsilyl group occurring under the acidic reaction conditions, although potassium fluoride was added to ensure complete removal. The reaction sequence (Scheme 7) gave the ketone (24) in 36% overall yield from (6), somewhat poorer than the preparation of compound (23) from (6) *via* the methoxyindene (1a). The ketone (24) is a colourless oil, characterised as its orange 2,4-dinitrophenylhydrazone.

(*c*) *With dichloroketene.* When dichloroacetyl chloride was added to a solution of the 3a*H*-indene (1b) in ether containing excess of triethylamine, the dichloroketene generated [19]

reacted with the indene. Chromatographic work-up gave the trienone (26) in moderate yield (Scheme 8). Attempts to isolate the initial adduct (25) were not successful, although in one case, n.m.r. analysis of the crude reaction mixture prior to chromatography indicated that (26) was not present at that stage. The trienone (26) is presumably formed on chromatography.

Conclusion

The cycloaddition reactions of the 3a*H*-indene (1a) have now been extended to other dienophiles. In contrast to the reactions with maleic anhydride and *N*-phenylmaleimide which gave isolable [4 + 2]-adducts, 2-chloroacryloyl chloride and 2-chloroacrylonitrile give only [8 + 2]-adducts. The use of the trimethylsiloxy 3a*H*-indene derivative (1b) offers some advantages over the methoxy analogue (1a) in certain cases. In subsequent papers we will describe the conversion of these cycloadducts into tricyclic [10]annulene derivatives.

Experimental

I.r. spectra were recorded for liquids as thin films and for solids as solutions in carbon tetrachloride on a Perkin-Elmer 298 spectrophotometer, and calibrated against polystyrene. U.v. spectra were recorded on a Pye Unicam SP 800B spectrophotometer. ^{1}H N.m.r. spectra were recorded on a Bruker WM 250 (operating at 250 MHz), on a Perkin-Elmer R 32 (operating at 90 MHz), or on a Varian EM 360 spectrometer (operating at 60 MHz). Mass spectra were recorded using a VG Micromass 7070B mass spectrometer operating at 70 eV using a direct insertion probe. Silica gel H (Merck, type 60) was used for column chromatography, pressure being applied at 5—10 lb in^{-2}. Ether refers to diethyl ether, and petroleum refers to light petroleum, b.p. 40—60 °C, unless otherwise stated. All solvents were dried by standard procedures.

Reductive Alkylation of Indan-1-one.—(*a*) Indan-1-one (4) (15.0 g) was reduced and methylated using the conditions described previously.[1] Chromatography on silica gel (Hopkin and Williams MFC, 500 g) eluting with light petroleum (b.p. 60—80 °C) containing an increasing proportion of ether gave (i) 2,7a-dimethyl-2,3,5,7a-tetrahydro-1*H*-inden-1-one [1] (7) (1.0 g, 6%). (ii) A mixture from which crystallised 2-*indan*-1-*yl*-2-*methylindan*-1-*one* (9) (0.72 g, 5%), m.p. 117.5—118.5 °C (from light petroleum, b.p. 60—80 °C) (Found: C, 87.1; H, 7.0. $C_{19}H_{18}O$ requires C, 87.0; H, 6.9%); $\nu_{max.}$ 1 710, 1 602, and 1 280 cm^{-1}; δ_H (90 MHz, CCl_4) 1.24 (3 H, s, 2-Me), 1.7—2.45 (2 H, m, 2 × 2′-H), 2.5—3.0 (4 H, m, 2 × 3-H and 2 × 3′-H), 3.78 (1 H, t, *J* 9 Hz, 1′-H), 6.5—7.1 (4 H, m, 4′-7′-H), and 7.1—7.9 (4 H, m, 4—7-H); *m/z* 262 (M^+), 146, and 117 (base). The residual liquid (4.8 g) was a 2 : 1 mixture of 7a-methyl-2,3,5,7a-tetrahydro-1*H*-inden-1-one [1] (5) (18%) and 2,2-dimethylindanone (9%). (iii) 2-Methylindan-1-one (0.5 g, 3%). (iv) 1,1′-Dihydroxybi-indan-1-yl (8) (0.4 g, 2.5%), m.p. 158—161 °C (lit.,[20] m.p. 156—157 °C). (v) Indan-1-ol (1.1 g, 7%).

(*b*) *Large-scale preparation of* 7a-*methyl*-2,3,5,7a-*tetrahydro*-1H-*inden*-1-*one* (5). A solution of indan-1-one (118 g, 0.89 mol) and t-butyl alcohol (150 g, 2.03 mol) in dry tetrahydrofuran (400 ml) was added dropwise during 1 h to a stirred solution of potassium (100 g, 2.55 g atom) in liquid ammonia (5 l) at −78 °C. A solution of anhydrous lithium bromide (206 g, 2.34 mol) in dry tetrahydrofuran (600 ml) was added, followed after 0.5 h by a simultaneous rapid addition of aqueous tetrahydrofuran (50%; 900 ml) and iodomethane (134 g, 0.94 mol). The external cooling was removed, and the ammonia allowed to evaporate overnight. Water (2 l) was added, and the mixture was extracted with ether (3 × 800 ml). The combined ether extracts were washed with water (2 × 500 ml), dried (Na_2SO_4) and evaporated. The resulting oil was distilled, and the fraction boiling in the range 85—95 °C/7 mmHg was collected as a colourless oil (82.8 g). Analysis of a small portion of this oil showed that it contained 84% of the title compound, hence the yield of (5) was 69.9 g (53%). The distilled material was used without further purification.

Improved Preparation of 5,7a-*Dihydro*-7a-*methyl*-1H-*inden*-1-*one* (6).—Chlorotrimethylsilane (82 g, 0.75 mol) was added to a stirred solution of sodium iodide (115 g, 0.77 mol) in dry acetonitrile (600 ml) at room temperature under nitrogen. After 5 min, a mixture of 7a-methyl-2,3,5,7a-tetrahydro-1*H*-inden-1-one (5) (84% pure; 91 g, 0.52 mol) and dry triethylamine (76 g, 0.75 mol) was added during 30 min. The mixture was warmed to 45 °C for 2 h, cooled and extracted with petroleum (4 × 150 ml). The combined extracts were evaporated, and the residue distilled to give 3a,6-*dihydro*-3a-*methyl*-3-*trimethylsiloxy*-1H-*indene* (10) (117 g, 97%) as a mobile oil, b.p. 82—85 °C/3 mmHg (Found: C, 71.3; H, 9.5. $C_{13}H_{20}OSi$ requires C, 70.85; H, 9.15%); δ_H (90 MHz; CCl_4) 0.23 (9 H, s, $SiMe_3$), 1.11 (3 H, s, 3a-Me), 2.5—2.9 (3 H, m), 2.9—3.3 (1 H, m), 4.51 (1 H, m, 2-H), 5.2—5.6 (1 H, m), 5.6—5.9 (1 H, m), and 5.9—6.1 (1 H, br d, *J* 10 Hz, 4-H). A stirred solution of this trimethylsilyl ether (55 g, 0.25 mol) in dry tetrahydrofuran (300 ml) was treated with a solution of phenylselenyl bromide [prepared at 0 °C from diphenyl diselenide (39.3 g, 0.125 mol) and bromine (20.0 g, 0.125 g atom)] in tetrahydrofuran (300 ml) at −78 °C during 2 h. The resulting mixture was allowed to warm to −30 °C during 1 h, poured into saturated sodium hydrogencarbonate solution, and extracted with ether (3 × 250 ml). The combined extracts were washed with water (500 ml), dried ($MgSO_4$), and evaporated to give the selenide (11) (79.4 g). The selenide was dissolved in tetrahydrofuran (650 ml), pyridine (35 g) was added, and the solution was cooled to 5 °C. Hydrogen peroxide (30%; 85 g, 0.75 mol) was added dropwise so as to maintain the temperature between 5 and 10 °C. The mixture was poured into water and extracted with ether. The ether extracts were washed with water, dried, and evaporated to an oil. Chromatography on silica gel using petroleum containing an increasing proportion of ether gave the title compound (6) [1] [21.4 g, 57% from (5)].

During an earlier run from the dienone (5) (5.0 g) further elution of the column with ether gave (*E*)-2-methylcinnamic acid (0.97 g, 18%), m.p. 175—177 °C (from chloroform–petroleum) (lit.,[21] m.p. 176—178 °C).

Cycloaddition Reactions of 3-*Methoxy*-3a-*methyl*-3aH-*indene* (1a).—The 3a*H*-indene (1a) was generated in 1,2-dimethoxyethane from the trienone (6) as previously described.[1]

(*a*) *With* N-*phenylmaleimide*. A solution of *N*-phenylmaleimide (0.63 g, 3.6 mmol) in dry 1,2-dimethoxyethane (3 ml) was added to a solution of the 3a*H*-indene (1a) [from the trienone (6) (0.50 g, 3.4 mmol)]. The solution was allowed to warm to room temperature, filtered through Celite, and evaporated. The residue was chromatographed on silica gel using petroleum–dichloromethane (1 : 1) to give the *endo*-[4 + 2]-adduct (12a) (0.54 g, 47%), m.p. 99—100 °C (from light petroleum, b.p. 60—80 °C) (lit.,[1] m.p. 91—93 °C); δ_H (250 MHz; $CDCl_3$) 0.90 (3 H, s, 7a-Me), 3.30 (1 H, d, *J* 8.5 Hz, 8-H), 3.65 (1 H, d, *J* 8.5 Hz, 9-H), 3.74 (3 H, s, OMe), 6.00 (1 H, dd, $J_{5,6}$ 5.2 Hz, $J_{6,7}$ 9.9 Hz, 6-H), 6.10 (1 H, dd, $J_{5,6}$ 5.2 Hz, $J_{4,5}$ 9.0 Hz, 5-H), 6.18 (1 H, d, *J* 9.9 Hz, 7-H), 6.19

(1 H, d, *J* 6.0 Hz, 3-H), 6.26 (1 H, d, *J* 6.0 Hz, 2-H), 6.43 (1 H, d, *J* 9.0 Hz, 4-H), and 7.1—7.5 (5 H, m, Ph).

Thermal rearrangement of the adduct (12a). The adduct (12a) (195 mg) was heated to 110 °C under a water-pump vacuum for 2 h. Chromatography of the resulting viscous oil on silica gel eluting with petroleum containing an increasing proportion of dichloromethane–ether (3 : 1 v/v) gave (i) the *exo*-[8 + 2]-adduct (13a) [1] (66 mg, 34%), δ_H (250 MHz; $CDCl_3$) 0.91 (3 H, s, 7b-Me), 2.82 (1 H, dd, $J_{1,2}$ 10 Hz, $J_{1,7a}$ 7 Hz, 1-H), 2.98 (2 H, m, 2- and 7a-H), 3.57 (3 H, s, OMe), 6.01 (1 H, d, *J* 5 Hz, 5-H), 6.17 (2 H, m, 6- and 7-H), 6.42 (1 H, d, *J* 5 Hz, 4-H), 6.84 (1 H, d, *J* 5 Hz, 3-H), and 7.2—7.6 (5 H, m, Ph). Irradiation at δ 2.82 simplifies the multiplet at δ 6.17 to give δ 6.16 (1 H, dd, $J_{5,6}$ 5 Hz, $J_{6,7}$ 10 Hz, 6-H) and δ 6.18 (1 H, d, $J_{6,7}$ 10 Hz, 7-H). (ii) The *endo*-[8 + 2]-adduct (14a) [1] (89 mg, 46%), δ_H (250 MHz; $CDCl_3$) 0.92 (3 H, s, 7b-Me), 3.20 (1 H, dd, $J_{1,7a}$ 10 Hz, $J_{7,7a}$ 6.5 Hz, 7a-H), 3.54 (3 H, s, OMe), 3.56 (1 H, d, *J* 9 Hz, 2-H), 3.62 (1 H, dd, $J_{1,2}$ 9 Hz, $J_{1,7a}$ 10 Hz, 1-H), 5.90 (1 H, d, *J* 5 Hz, 5-H), 6.16 (1 H, dd, $J_{6,7}$ 9 Hz, $J_{7,7a}$ 6.5 Hz, 7-H), 6.24 (1 H, dd, $J_{5,6}$ 5 Hz, $J_{6,7}$ 9 Hz, 6-H), 6.38 (1 H, d, *J* 5 Hz, 4-H), 6.60 (1 H, d, *J* 5 Hz, 3-H), and 6.9—7.5 (5 H, m, Ph).

(*b*) *With maleic anhydride*. A solution of maleic anhydride (0.45 g, 4.6 mmol) in dry 1,2-dimethoxyethane (6 ml) was added to a solution of the 3a*H*-indene (1a) [from the trienone (6) (1.0 g, 6.8 mmol)]. The mixture was allowed to warm to 0 °C, filtered, and evaporated at 0 °C/2 mmHg. The residue was dissolved in dichloromethane (50 ml) containing acetic anhydride (0.5 ml) at 0 °C, and chromatographed on an ice–water jacketed silica gel column eluting with petroleum–dichloromethane containing acetic anhydride (0.5% v/v) to give the endo-[4 + 2]-*adduct* (12b) (1.00 g, 57%) as an unstable crystalline solid, δ_H (250 MHz; $CDCl_3$) 0.87 (3 H, s, 7a-Me), 3.41 (1 H, d, *J* 8.5 Hz, 8-H), 3.71 (3 H, s, OMe), 3.72 (1 H, d, *J* 8.5 Hz, 9-H), 6.02 (1 H, dd, $J_{5,6}$ 5.2 Hz, $J_{6,7}$ 9.0 Hz, 6-H), 6.12 (1 H, dd, $J_{4,5}$ 9.4 Hz, $J_{5,6}$ 5.2 Hz, 5-H), 6.16 (1 H, d, *J* 9.0 Hz, 7-H), 6.26 (1 H, d, *J* 6.0 Hz, 3-H), 6.37 (1 H, d, *J* 6.0 Hz, 2-H), and 6.43 (1 H, d, *J* 9.4 Hz, 4-H).

Thermal rearrangement of the adduct (12b). The adduct (12b) (0.81 g) was heated at 50 °C under a water-pump vacuum for 30 min. Chromatography on silica gel, eluting with petroleum containing acetic anhydride (*ca.* 0.1% v/v) and an increasing proportion of ether gave (i) the exo-[8 + 2]-*adduct* (13b) (0.19 g, 23%), as an oil, $\nu_{max.}$ (CCl_4) 1 860, 1 782, 1 736, 1 076, and 912 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 0.90 (3 H, s, 7b-Me), 2.92 (1 H, dd, $J_{1,2}$ 9.6 Hz, $J_{1,7a}$ 7.4 Hz, 1-H), 2.98 (1 H, dd, $J_{1,7a}$ 7.4 Hz, $J_{7,7a}$ 5.7 Hz, 7a-H), 3.13 (1 H, dd, *J* 9.6 Hz, 2-H), 3.55 (3 H, s, OMe), 6.02 (1 H, d, *J* 5.0 Hz, 5-H), 6.11 (1 H, dd, $J_{6,7}$ 9.1 Hz, $J_{7,7a}$ 5.7 Hz, 7-H), 6.19 (1 H, dd, $J_{5,6}$ 5.0 Hz, $J_{6,7}$ 9.1 Hz, 6-H), 6.46 (1 H, d, *J* 5.8 Hz, 4-H), and 6.76 (1 H, d, *J* 5.8 Hz, 3-H); *m/z* 258 (M^+). (ii) the endo-[8 + 2]-*adduct* (14b) (0.28 g, 35%), as an oil (Found: *m/z* 258.0888. $C_{15}H_{14}O_4$ requires 258.0892); $\nu_{max.}$ (CCl_4) 1 860, 1 782, 1 736, 1 074, and 916 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 0.86 (3 H, s, 7b-Me), 3.18 (1 H, $J_{1,7a}$ 9.9 Hz, $J_{7,7a}$ 6.4 Hz, 7a-H), 3.52 (3 H, s, OMe), 3.64 (1 H, d, *J* 9.8 Hz, 2-H), 3.78 (1 H, dd, $J_{1,2}$ 9.8 Hz, $J_{1,7a}$ 9.9 Hz, 1-H), 5.91 (1 H, d, *J* 5.3 Hz, 5-H), 6.06 (1 H, dd, $J_{6,7}$ 9.0 Hz, $J_{7,7a}$ 6.4 Hz, 7-H), 6.31 (1 H, dd, $J_{5,6}$ 5.3 Hz, $J_{6,7}$ 9.0 Hz, 6-H), 6.41 (1 H, d, *J* 5.6 Hz, 4-H), and 6.57 (1 H, d, *J* 5.6 Hz, 3-H); *m/z* 258 (M^+), 160, and 145 (base).

Thermal rearrangement of the adduct (12b) *in the presence of* N-*phenylmaleimide*. A solution of the adduct (12b) (90 mg, 0.35 mmol) and *N*-phenylmaleimide (60 mg, 0.35 mmol) in dichloromethane (2 ml) was heated under reflux for 15 min. The solvent was evaporated and the residue chromatographed to give (i) a mixture of the *exo*-[8 + 2]-adduct (13b) and unchanged *N*-phenylmaleimide (55 mg). (ii) A 2 : 1 mixture of the *endo*-[4 + 2]-*N*-phenylmaleimide adduct (12a) and the *endo*-[8 + 2]-maleic anhydride adduct (14b) (29 mg).

Thermal rearrangement of the adduct (12b) *in the presence of cyclopentadiene*. A solution of the adduct (12b) (121 mg, 0.47 mmol) in ether (5 ml) was treated with a solution of cyclopentadiene (31 mg, 0.47 mmol) in ether (5 ml) at 0 °C. On being warmed to 30 °C under nitrogen, the mixture became bright yellow. T.l.c. showed the presence of the 3a*H*-indene (1a) as a fast running yellow spot.

(*c*) *With* 2-*chloroacrylonitrile*. A solution of freshly distilled 2-chloroacrylonitrile (4.0 g, 46 mmol) in dry 1,2-dimethoxyethane (24 ml) was added to a solution of the 3a*H*-indene (1a) [from the trienone (6) (3.0 g, 21 mmol)]. The mixture was heated to 70 °C for 1 h, filtered, and evaporated. The residue was chromatographed on silica gel; elution with petroleum containing an increasing proportion of ether gave (i) a 3 : 1 mixture of 2-*chloro*-2-*cyano*-2a-*methoxy*-7b-*methyl*-2,2a,7a,7b-*tetrahydro*-1H-*cyclopent*[cd]*indene* (15) and its *isomer* (16) (2.8 g, 55%). Cooling of this mixture to 0 °C gave crystals of the *exo* adduct (15) (1.5 g); m.p. 82—84 °C (from light petroleum, b.p. 60—80 °C) (Found: C, 67.8; H, 5.7; N, 5.6. $C_{14}H_{14}ClNO$ requires C, 67.9; H, 5.7; N, 5.65%); $\lambda_{max.}$ (EtOH) 305 nm (log ε 3.84); δ_H (250 MHz, $CDCl_3$) 0.92 (3 H, s, 7b-Me), 1.88 (1 H, dd, $J_{1\alpha,1\beta}$ 13.2 Hz, $J_{1\alpha,7a}$ 12.4 Hz, 1-H_α), 2.41 (1 H, dd, $J_{1\alpha,1\beta}$ 13.2 Hz, $J_{1\beta,7a}$ 5.2 Hz, 1-H_β), 2.83 (1 H, ddd, $J_{1\beta,7a}$ 5.2 Hz, $J_{1\alpha,7a}$ 12.4 Hz, $J_{7,7a}$ 5.8 Hz, 7a-H), 3.55 (3 H, s, 2a-OMe), 5.80—5.95 (2 H, m, 5- and 7-H), 6.14 (1 H, dd, $J_{5,6}$ 5.0 Hz, $J_{6,7}$ 9.0 Hz, unaffected by decoupling of 7a-H, 6-H), 6.57 (1 H, d, $J_{3,4}$ 5.7 Hz, 3- or 4-H), and 6.71 (1 H, d, $J_{3,4}$ 5.7 Hz, 3- or 4-H). The *endo*-adduct (16) gives δ_H (250 MHz; $CDCl_3$) 0.95 (3 H, s, 7b-Me), 1.78 (1 H, t, $J_{1\alpha,1\beta}$ and $J_{1\alpha,7a}$ 12.4 Hz, 1-H_α), 2.61 (1 H, dd, $J_{1\alpha,1\beta}$ 12.4 Hz, $J_{1\beta,7a}$ 5.5 Hz, 1-H_β), 2.71 (1 H, ddd, $J_{1\beta,7a}$ 5.5 Hz, $J_{1\alpha,7a}$ 12.4 Hz, $J_{7,7a}$ 5.8 Hz, 7a-H), 3.61 (3 H, s, 2a-OMe), 5.80—5.92 (2 H, m, 5- and 7-H), 6.12 (1 H, dd, $J_{5,6}$ 5.0 Hz, $J_{6,7}$ 9.0 Hz, unaffected by decoupling of 7a-H, 6-H), 6.43 (1 H, d, $J_{3,4}$ 5.7 Hz, 3- or 4-H), and 6.68 (1 H, d, $J_{3,4}$ 5.7 Hz, 3- or 4-H). (ii) A 3 : 2 mixture of the 1-*chloro*-1-*cyano*-3-*methoxy*-7b-*methyl*-2,2a,7a,7b-*tetrahydro*-1H-*cyclopent*[cd]*indene* (18a) and its 3-*methyl derivative* (18b) (0.9 g, 17%); δ_H (250 MHz; $CDCl_3$) of adduct (18a) 0.96 (3 H, s, 7b-Me), 2.43 (1 H, d, *J* 15.1 Hz, 2-H_β), 7a-H), 2.78 (1 H, d, *J* 15.1 Hz, 2-H_α), 3.03 (1 H, br d. $J_{7,7a}$ 5.9 Hz, 7a-H), 3.39 (3 H, s, 2.78 (1 H, d, *J* 15.1 Hz, 2-H_α), 5.83 (1 H, d, $J_{5,6}$ 5.4 Hz, 5-H), 5.90 (1 H, dd, $J_{6,7}$ 9.2 Hz, $J_{7,7a}$ 5.9 Hz, becomes d on decoupling of 7a-H, 7-H), 6.44 (2 H, s, 3- and 4-H), 6.45 (1 H, ddd, $J_{5,6}$ 5.4 Hz, $J_{6,7}$ 9.2 Hz, $J_{6,7a}$ 0.9 Hz, the fine splitting is removed by decoupling of 7a-H, 6-H), and of adduct (18b) 0.99 (3 H, s, 7b-Me), 1.93 (3 H, s, 3-Me), 2.37 (1 H, d, *J* 15.4 Hz, 2-H_β), 2.69 (1 H, d, *J* 15.4 Hz, 2-H_α), 3.01 (1 H, br d, $J_{7,7a}$ 6.7 Hz, 7a-H), 3.40 (3 H, s, 2a-OMe), 5.69 (1 H, d, $J_{5,6}$ 5.1 Hz, 5-H), 5.83 (1 H, dd, $J_{6,7}$ 9.3 Hz, $J_{7,7a}$ 6.7 Hz, 7-H), 6.19 (1 H, s, sharpened by decoupling of 3-Me, 4-H), and 6.43 (1 H, ddd, $J_{5,6}$ 5.1 Hz, $J_{6,7}$ 9.3 Hz, $J_{6,7a}$ 0.9 Hz, the fine splitting is removed by irradiation of 7a-H, 6-H).

Conversion of the nitrile (15) *into the aldehyde* (17). A solution of the *exo*-2-chloroacrylonitrile adduct (15) (130 mg, 0.53 mmol) in dry tetrahydrofuran (5 ml) under nitrogen at room temperature was treated with a solution of di-isobutylaluminium hydride (1M; 1.0 ml, 1.0 mmol). The mixture was stirred for 1.5 h. Methanol (1.5 ml) was then added, followed by water (2 ml). The resulting slurry was extracted with ether (2 × 30 ml), the combined extracts dried ($MgSO_4$), the solvent evaporated and the residue chromatographed on silica gel. Elution with 20% ether in petroleum gave the 2-*chloro*-2a-*methoxy*-7b-*methyl*-2,2a,7a,7b-*tetrahydro*-1H-*cyclopent*-[cd]*indene*-2-*carbaldehyde* (17) (36 mg, 28%), as an oil; δ_H (250 MHz, $CDCl_3$) 0.92 (3 H, s, 7b-Me), 2.00 (1 H, dd,

$J_{1\alpha,1\beta}$ 13.9 Hz, $J_{1\alpha,7a}$ 7.0 Hz, 1-H$_\beta$), 2.02 (1 H, dd, $J_{1\alpha,1\beta}$ 13.9 Hz, $J_{1\alpha,7a}$ 11.4 Hz, 1-H$_\alpha$), 2.89 (1 H, ddd, $J_{1\beta,7a}$ 7.0 Hz, $J_{1\alpha,7a}$ 11.4 Hz, $J_{7,7a}$ 6.0 Hz, 7a-H), 3.40 (3 H, s, 2a-OMe), 5.84 (1 H, d, $J_{5,6}$ 4.9 Hz, 5-H), 5.92 (1 H, dd, $J_{6,7}$ 9.2 Hz, $J_{7,7a}$ 6.0 Hz, 7-H), 6.11 (1 H, dd, $J_{5,6}$ 4.9 Hz, $J_{6,7}$ 9.2 Hz, 6-H), 6.17 (1 H, d, *J* 5.5 Hz, 3-H), 6.60 (1 H, d, *J* 5.5 Hz, 4-H), and 9.60 (1 H, s, CHO).

Conversion of the nitriles (18a) *and* (18b) *into the aldehydes* (19a) *and* (19b). A stirred solution of a 3 : 2 mixture of the 2-chloroacrylonitrile adducts (18a) and (18b) (204 mg, 0.82 mmol) in hexane (10 ml) and dry tetrahydrofuran (2 ml) at 0 °C under nitrogen was treated with a solution of di-isobutylaluminium hydride (1M; 2.0 ml, 2.0 mmol). The mixture was stirred at room temperature for 2 h and methanol (2 ml) was added followed by water (4 ml). The mixture was filtered and the residue washed with ether (3 × 10 ml). The filtrate was extracted with ether (3 × 15 ml), the combined extracts and washings dried ($MgSO_4$), the solvent evaporated and the residue chromatographed on silica gel. Elution with 25% ether in petroleum gave a 2 : 1 mixture of 1-*chloro*-2a-*methoxy*-7b-*methyl*-2,2a,7a,7b-*tetrahydro*-1H-*cyclopent*[cd]*indene*-1-*carbaldehyde* (19a) and its 3-*methyl derivative* (19b) (36 mg, 17%), as an oil; the aldehyde derived from adduct (18a) gives δ_H (250 MHz; $CDCl_3$) 0.93 (3 H, s, 7b-Me), 2.07 (1 H, d, *J* 14.0 Hz, 2-H$_\beta$), 2.68 (1 H, d, *J* 14.0 Hz, 2-H$_\alpha$), 3.00 (1 H, br d, $J_{7,7a}$ 6.4 Hz, 7a-H), 3.39 (3 H, s, OMe), 5.69 (1 H, dd, $J_{6,7}$ 9.2 Hz, $J_{7,7a}$ 6.4 Hz, 7-H), 5.87 (1 H, d, $J_{5,6}$ 5.2 Hz, 5-H), 6.36 (1 H, ddd, $J_{5,6}$ 5.2 Hz, $J_{6,7}$ 9.2 Hz, $J_{6,7a}$ 1.1 Hz, the fine splitting is removed by decoupling of 7a-H, 6-H), 6.45 (1 H, d, *J* 5.9 Hz, 4-H), 6.47 (1 H, d, *J* 5.9 Hz, 3-H), and 9.43 (1 H, s); the aldehyde derived from adduct (18b) gives δ_H (250 MHz; $CDCl_3$) 0.96 (3 H, s, 7b-Me), 1.94 (3 H, s, 3-Me), 2.00 (1 H, d, *J* 14.5 Hz, 2-H$_\beta$), 2.62 (1 H, d, *J* 14.5 Hz, 2-H$_\alpha$), 3.00 (1 H, br d, $J_{7,7a}$ 6.4 Hz, 7a-H), 3.35 (3 H, s, OMe), 5.61 (1 H, dd, $J_{6,7}$ 9.2 Hz, $J_{7,7a}$ 6.4 Hz, 7-H), 5.72 (1 H, d, $J_{5,6}$ 5.2 Hz, 5-H), 6.20 (1 H, s, 4-H), 6.35 (1 H, ddd, $J_{5,6}$ 5.2 Hz, $J_{6,7}$ 9.2 Hz, $J_{6,7a}$ 1.1 Hz, the fine coupling is removed by decoupling of 7a-H, 6-H), and 9.48 (1 H, s).

Flash vacuum pyrolysis of the adducts (15) *and* (16). A 2 : 3 mixture of the adducts (15) and (16) (98 mg) was distilled at 0.3 mmHg through a tube heated to 500 °C. Examination of the pyrolysate (66 mg) by n.m.r. spectroscopy showed it to be a 2 : 3 : 3 mixture of the adducts (15) and (16), and 1-methoxy-1-methyl-1*H*-indene.

(*d*) *With 2-chloroacryloyl chloride.* A solution of 2-chloroacryloyl chloride [16] (4.2 g, 34 mmol) in dry 1,2-dimethoxyethane (10 ml) was added to a solution of the 3a*H*-indene (1a) [from the trienone (6) (4.75 g, 32 mmol)]. The mixture was allowed to warm to 0 °C, filtered, and the residue washed with 1,2-dimethoxyethane (20 ml). The combined filtrate and washings (3.3%) were treated with a mixture of methanol (2 ml) and triethylamine (1 ml) and the mixture was stirred at room temperature for 1 h. The solvent was evaporated and the residue chromatographed on silica gel. Elution with 20% ether in petroleum gave *methyl* 2-*chloro*-2a-*methoxy*-7b-*methyl*-2,-2a,7a,7b-*tetrahydro*-1H-*cyclopent*[cd]*indene*-2-*carboxylate* (21) containing 1 part in 25 of its *isomer* (22) (145 mg, 48%), as an oil; δ_H (250 MHz; $CDCl_3$) 0.92 (3 H, s, 7b-Me), 2.09 (1 H, dd, $J_{1\alpha,1\beta}$ 14.0 Hz, $J_{1\alpha,7a}$ 12.4 Hz, 1-H$_\alpha$), 2.22 (1 H, dd, $J_{1\alpha,1\beta}$ 14.0 Hz, $J_{1\beta,7a}$ 5.5 Hz, 1-H$_\beta$), 2.79 (1 H, ddd, $J_{1\alpha,7a}$ 12.4 Hz, $J_{1\beta,7a}$ 5.5 Hz, $J_{7,7a}$ 6.3 Hz, 7a-H), 3.57 (3 H, s, 2a-OMe), 3.76 (3 H, s, CO_2Me), 5.80 (1 H, d, *J* 5.2 Hz, 5-H), 5.91 (1 H, dd, $J_{7,7a}$ 6.3 Hz, $J_{6,7}$ 9.4 Hz, 7-H), 6.08 (1 H, dd, $J_{5,6}$ 5.2 Hz, $J_{6,7}$ 9.4 Hz, 6-H), 6.26 (1 H, d, *J* 5.7 Hz, 3- or 4-H), and 6.54 (1 H, d, *J* 5.7 Hz, 3- or 4-H); the minor isomer (22) gives extra peaks at δ 0.87 (3 H, s, 7b-Me), 3.05 (1 H, ddd, 7a-H), 3.44 (3 H, s, 2a-OMe), 3.81 (3 H, s, CO_2Me), 5.84 (1 H, d, 5-H), 6.49 (1 H, d, 3- or 4-H), and 6.61 (1 H, d, 3- or 4-H); *m*/*z* 280 (M^+), 160 (base), and 145. The remainder of the solution of the adduct (96.7%) was treated as described below to give the ketone (23) (2.65 g, 42%).

Conversion of the ester (21) *into the aldehyde* (17). A solution of the ester (21) (83.2 mg, 0.30 mmol) in petroleum (8 ml) was stirred at 0 °C under nitrogen, and treated with a solution of di-isobutylaluminium hydride in hexane (1M; 1 ml, 1 mmol). After 30 min, methanol (1.5 ml) was added followed by water (2 ml), and the mixture stirred at room temperature for 1 h. The mixture was filtered, the residue washed with ether (2 × 20 ml), and the filtrate extracted with ether (2 × 30 ml). The combined washings and extracts were dried (Na_2SO_4) and evaporated to an oil. Chromatography gave the intermediate alcohol (51.4 mg, 69%), $\nu_{max.}$ 3 440 cm^{-1}. The alcohol (39 mg, 0.155 mmol) in dichloromethane (5 ml) was treated with a solution prepared from powdered chromium trioxide (78 mg, 0.78 mmol) in pyridine (125 mg, 1.7 mmol) and dichloromethane (2 ml). After 10 min at room temperature, the solvent was removed, the mixture filtered, and the residue washed with ether (2 × 25 ml). The combined filtrate and washings were concentrated, and the residue chromatographed on silica gel. Elution with petroleum–ether (3 : 1 v/v) gave the aldehyde (17), identical with the previous sample.

Preparation of 2a-*methoxy*-7b-*methyl*-1,2a,7a,7b-*tetrahydro*-2H-*cyclopent*[cd]*inden*-2-*one* (23). To a mechanically stirred suspension of potassium hydride (from a dispersion in oil, 25%; 46 g, 0.23 mol) in dry 1,2-dimethoxyethane (100 ml) under nitrogen and cooled externally by a cooling bath at −23 °C was added a solution of 18-crown-6 (37.5 g, 0.14 mol) in dry 1,2-dimethoxyethane (160 ml), followed by a solution of 5,7a-dihydro-7a-methyl-1*H*-inden-1-one (6) (18.7 g, 0.13 mol) in dry 1,2-dimethoxyethane (20 ml). After 0.5 h, freshly distilled methyl fluorosulphonate (12 ml, 0.15 mol) was added followed by 2-chloroacryloyl chloride (20.0 g, 0.16 mol). The solution was allowed to warm to 0 °C, filtered and the residue washed with dry 1,2-dimethoxyethane (80 ml). Sodium azide (32 g, 0.48 mol) was added to the filtrate. The mixture was stirred in a sealed system at room temperature for 16 h, filtered and the filtrate refluxed for 2 h. The resulting dark brown mixture was cooled to room temperature, treated with 2 : 1 acetic acid–water (200 ml) and warmed at 60 °C for 1 h. The cooled mixture was poured into water (1 l) and extracted with ether (4 × 250 ml). The combined ether layers were washed with water (500 ml), then saturated aqueous sodium hydrogen carbonate (2 × 500 ml), dried (Na_2SO_4), the solvent evaporated, and the residue chromatographed on silica gel. Elution with 30% ether in petroleum gave the *title ketone* (23) (12.5 g, 48%), as a colourless oil; $\nu_{max.}$ (neat) 1 732 (C=O stretch), 1 114 (m), and 1 052 cm^{-1} (m); $\lambda_{max.}$ (EtOH) 240 (log ε 3.43), 310 (3.75) and 342sh nm (3.29); δ_H (250 MHz; $CDCl_3$) 1.12 (3 H, s, 7b-Me), 2.12 (1 H, dd, *J* 11.8, 18.6 Hz, 1-H), 2.50 (1 H, dd, *J* 7.8, 18.6 Hz, 1-H), 2.81 (1 H, ddd, *J* 7.8, 11.8, 6.1 Hz, 7a-H), 3.50 (3 H, s, 2a-OMe), 5.88 (2 H, m, 5- and 7-H), 6.02 (1 H, dd, $J_{5,6}$ 5.2 Hz, $J_{6,7}$ 9.4 Hz, 6-H), 6.24 (1 H, d, *J* 5.7 Hz, 3- or 4-H), and 6.47 (1 H, d, *J* 5.7 Hz, 3- or 4-H); *m*/*z* 202 (M^+), 160, 159, 145 (base), and 115.

Generation of 3a-*Methyl*-3-(*trimethylsiloxy*)-3aH-*indene* (1b).—Chlorotrimethylsilane (0.16 ml, 1.3 mmol) was added to a stirred solution of sodium iodide (200 mg, 1.3 mmol) in dry acetonitrile (1 ml) under nitrogen. A mixture of the trienone (6) (150 mg, 1.03 mmol) and dry triethylamine (0.17 ml, 1.3 mmol) was added and the resulting mixture was stirred at 35 °C for 1 h. The product was extracted with petroleum (3 × 3 ml) and the bright yellow combined extracts were concentrated under a reduced pressure of nitrogen at room temperature. The residue was chromatographed on silica gel. Elution with 5% ether in petroleum gave the *title compound*

(1b) (151 mg, 67%), as an unstable yellow oil; δ_H (250 MHz; $CDCl_3$) 0.28 (9 H, s, $SiMe_3$), 1.31 (3 H, s, 3a-Me), 5.05 (1 H, d, *J* 2.6 Hz, 2-H), 5.73 (1 H, dd, *J* 5.1 Hz, 9.0 Hz, with other fine splittings, 5- or 6-H), 5.81 (1 H, dd, *J* 5.1, 9.1 Hz with other fine splittings, 5- or 6-H), 6.13 (1 H, m, 1-H), 6.24 (1 H, d, with fine splittings, *J* 9.1 Hz, 4- or 7-H), and 6.31 (1 H, d with fine splittings, *J* 9.0 Hz, 4- or 7-H).

Thermal rearrangement of the 3aH-*indene* (1b). A solution of the 3a*H*-indene (1b) [prepared from the trienone (6) (122 mg) by the method described above] in benzene (5 ml) was refluxed under nitrogen for 15 min. The mixture was cooled to room temperature, the solvent evaporated and the residue chromatographed on silica. Elution with 5% ether in petroleum gave 1-*methyl*-1-(*trimethylsiloxy*)-1H-*indene* (65 mg, 37%) as an oil; δ_H (90 MHz; $CDCl_3$) 0.12 (9 H, s, $SiMe_3$), 1.63 (3 H, s, 1-Me), 6.36 (1 H, d, *J* 6 Hz), 6.61 (1 H, d, *J* 6 Hz), and 7.1—7.5 (4 H, m). To a solution of this trimethylsilyl ether (48 mg, 0.22 mmol) in tetrahydrofuran (2 ml) and water (0.5 ml) containing potassium fluoride (100 mg, 1.4 mmol) was added a solution of tetra-n-butylammonium hydroxide in methanol (25% w/v; 2 drops) and the resulting mixture refluxed for 2 h. The mixture was then poured into water (10 ml) and the product extracted with ether (3 × 4 ml). The combined extracts were washed with water (10 ml), dried (Na_2SO_4), the solvent evaporated and the residue chromatographed on silica. Elution with 40% ether in petroleum gave 1-methyl-1*H*-inden-1-ol (16 mg, 50%), as silky needles, m.p. 96—98 °C (from cold petroleum) (lit.,[10] m.p. 96—98 °C); δ_H (90 MHz; $CDCl_3$) 1.59 (3 H, s), 6.34 (1 H, d, *J* 6 Hz), 6.63 (1 H, d, *J* 6 Hz), and 7.1—7.5 (4 H, m).

Cycloaddition Reactions of the 3aH-*Indene* (1b).—(*a*) *With dimethyl acetylenedicarboxylate.* A solution of the trienone (6) (200 mg, 1.37 mmol) in dry ether (2 ml) under nitrogen at 10 °C was treated with dry triethylamine (0.20 ml, 1.5 mmol) and then with trimethylsilyl trifluoromethanesulphonate (0.26 ml, 1.4 mmol) and the mixture stirred for 1 h. Dimethyl acetylenedicarboxylate (0.25 ml, 2.0 mmol) was added to the resulting yellow solution of the 3a*H*-indene (1b) and the mixture was stirred at 35 °C for 1 h. The solvent was evaporated and the residue taken up in methanol (1 ml). The solution was cooled in ice and concentrated sulphuric acid (1.5 ml) was added dropwise during 5 min. The mixture was stirred for 10 min and poured into ice–water (20 ml). The product was extracted with ether (3 × 10 ml); the combined ether layers were washed with water (20 ml), dried ($MgSO_4$), the solvent evaporated and the residue chromatographed on silica. Elution with 30% ether in petroleum gave the *annulene* (3) (201 mg, 54%), as a yellow oil which solidified on cooling, m.p. 49—50 °C (from light petroleum, b.p. 60—80 °C) (Found: C, 71.2; H, 5.3. $C_{16}H_{14}O_4$ requires C, 71.1; H, 5.2%).

(*b*) *With* 2-*chloroacryloyl chloride.* A stirred solution of the trienone (6) (1.0 g, 6.85 mmol) in dry 1,2-dimethoxyethane (25 ml) under nitrogen at 0 °C was treated with dry triethylamine (1.25 ml, 9.4 mmol) and then trimethylsilyl trifluoromethanesulphonate (1.4 ml, 7.6 mmol). After 1 h, a solution of 2-chloroacryloyl chloride (950 mg, 7.6 mmol) in dry 1,2-dimethoxyethane (2 ml) was added. The yellow colour of the 3a*H*-indene was discharged and, after 30 min, finely powdered sodium azide (2.0 g, 31 mmol) was added and the mixture stirred at room temperature for 6 h. The mixture was filtered and the filtrate refluxed for 2 h. The mixture was cooled to room temperature and 2 : 1 acetic acid–water (20 ml) was added. After 1 h at 55 °C, potassium fluoride (4 g) was added. After a further 1 h at 55 °C, the mixture was poured into water (150 ml) and the product extracted with ether (4 × 60 ml). The combined ether layers were washed with water (100 ml), then saturated sodium hydrogen carbonate solution (2 × 100 ml), dried (Na_2SO_4), the solvent evaporated and the residue chromatographed on silica. Elution with 50% ether in petroleum gave 2a-*hydroxy*-7b-*methyl*-1,2a,7a,7b-*tetrahydro*-2H-*cyclopent*[cd]*inden*-2-*one* (24) (430 mg, 34%) as an oil; $\nu_{max.}$ (neat) 3 440 (br, OH stretch) and 1 734 cm^{-1} (C=O stretch); $\lambda_{max.}$ (EtOH) 307 (log ε 3.78) and 337sh nm (3.45); δ_H (250 MHz; $CDCl_3$) 1.10 (3 H, s, 7b-Me), 2.28 (1 H, dd, *J* 12.0, 16.8 Hz, 1-H), 2.47 (1 H, dd, *J* 7.0, 16.8 Hz, 1-H), 2.72 (1 H, ddd, *J* 7.0, 8.0, 12.0 Hz, 7a-H), 2.91 (1 H, br s, OH), 5.87 (2 H, m, 5- and 7-H), 5.97 (1 H, d, *J* 5.2 Hz, 3- or 4-H), 6.06 (1 H, dd, *J* 5.0 Hz, 8.9 Hz, 6-H), and 6.50 (1 H, d, *J* 5.2 Hz, 3- or 4-H); *m/z* 188 (M^+), 146 (base, $M^+ - CH_2{=}C{=}O$), 145, and 131.

Treatment of this ketone with 2,4-dinitrophenylhydrazine in ethanol acidified with sulphuric acid for 16 h at room temperature gave a precipitate of the 2,4-*dinitrophenylhydrazone* (35%), as orange crystals, m.p. 225—227 °C (from nitromethane) (Found: C, 58.6; H, 4.4; N, 15.2. $C_{18}H_{18}N_4O_6$ requires C, 58.7; H, 4.4; N, 15.2%).

(*c*) *With dichloroketene.* A stirred solution of the trienone (6) (400 mg, 2.7 mmol) in dry ether (4 ml) at 0 °C under nitrogen was treated with dry triethylamine (0.45 ml, 3.4 mmol) and then with trimethylsilyl trifluoromethanesulphonate (0.51 ml, 3.4 mmol). After 1 h at 0 °C, more dry triethylamine (0.45 ml, 3.4 mmol) was added. The mixture was warmed to reflux and a solution of dichloroacetyl chloride (500 mg, 3.4 mmol) in petroleum (4 ml) was added dropwise during 10 min. After further reflux for 30 min, the mixture was poured into water (20 ml) and the product extracted with ether (3 × 10 ml). The combined ether layers were washed with water (10 ml), dried (Na_2SO_4), the solvent evaporated and the residue chromatographed on silica gel. Elution with 30% ether in petroleum gave 7-*dichloroacetyl*-7,7a-*dihydro*-7a-*methyl*-1H-*inden*-1-*one* (26) (301 mg, 43%) as pale yellow prisms, m.p. 100—101 °C (from dichloromethane–petroleum) (Found: C, 55.9; H, 3.9; Cl, 27.4. $C_{12}H_{10}Cl_2O_2$ requires C, 56.05; H, 3.9; Cl, 27.6%); $\nu_{max.}$ (CCl_4) 1 712 cm^{-1} (C=O stretch); $\lambda_{max.}$ (EtOH) 241 (log ε 3.84) and 338 nm (3.82); δ_H (250 MHz; $CDCl_3$) 1.12 (3 H, s, 7a-Me), 4.09 (1 H, dd, *J* 1.2, 6.9 Hz, 7-H), 5.97 (1 H, s, $CHCl_2$), 6.13 (1 H, d, *J* 5.3 Hz, 4-H), 6.21 (1 H, dd, *J* 6.9, 9.3 Hz, 6-H), 6.45 (1 H, ddd, *J* 1.2, 5.3, 9.3 Hz, 5-H), 6.50 (1 H, d, *J* 5.4 Hz, 2-H), and 7.78 (1 H, d, *J* 5.4 Hz, 3-H); *m/z* 260, 258, 256 (1 : 6 : 9, M^+), 145 (base, $M^+ - Cl_2CHCO$), 117, 115, and 91.

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