3a*H*-Indenes. Part 5.[1] Preparation and Reactions of 3-Methoxy- and 3-Trimethylsiloxy-3a-substituted-3a*H*-indenes

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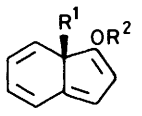
Previous work on the synthesis and cycloaddition of 3a-methyl-3a*H*-indenes (**1a**) and (**1b**) has been extended to substituents other than methyl at the ring junction. However, the increased migratory aptitudes of these substituents limits the scope of the 3a*H*-indene chemistry; thus rearrangement of 3a*H*-indenes (**1**) to their 1*H*-isomers (**2**) is sometimes so rapid that the 3a*H*-indenes could not be isolated or intercepted in cycloaddition reactions. Dissolving metal reduction and alkylation of indanone gave the dienones (**3**) where R = Et, Pr^i, $PhCH_2$, CH_2=$CHCH_2$, HC≡CCH_2, and MeO_2CCH_2, and these were converted into the trienones (**9**) *via* α-phenylselenation. The trienone (**9a**) was converted into the 3a*H*-indene (**1c**) which could be intercepted as the [8 + 2] cycloadduct (**10**). The 3a*H*-indenes (**1e**) and (**1h**) were similarly generated from the trienones (**9c**) and (**9g**), but rearranged too rapidly to the 1*H*-isomers (**2**) to be intercepted. The prop-2-ynyl derivative (**9e**) gave the 1*H*-isomer (**11**) directly on enolisation, and the allyl derivative (**9d**) also rearranged rapidly to give the indanone (**12**). Silylation of the isopropyl trienone (**9b**) with chlorotrimethylsilane generated the 3a*H*-indene (**1d**), but this underwent a rapid [1,5] shift of isopropyl at room temperature; with trimethylsilyl trifluoromethanesulphonate as the silylating agent at −23 °C, the 3a*H*-indene could be intercepted with PTAD to give the adduct (**15**) and with 2-chloroacryloyl chloride to give, after standard transformations, the tricyclic ketone (**17**). Similarly the methoxycarbonylmethyl (**9g**) and the hydroxyethyl (**22**) substituted trienones were converted into the tricyclic adducts (**18**), and (**24**) and (**25**), respectively.

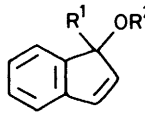
3a*H*-Indenes are bicyclic conjugated polyenes in which the peripheral conjugation is interrupted by an sp^3 carbon at the ring junction. We have recently reported the first preparation of a simple derivative of this system, the 3-methoxy-3a-methyl compound (**1a**), and have shown that it is an isolable but reactive species which readily undergoes sigmatropic rearrangement to the 1*H*-isomer (**2**) and participates in cycloaddition reactions to give both [4 + 2] and [8 + 2] adducts (Scheme 1).[2,3] The 3-trimethylsiloxy derivative (**1b**) behaves similarly,[3] and both compounds are of added interest because their [8 + 2] cycloadducts are easily converted into aromatic tricyclic [10]annulenes.[4,5]

We have now investigated the preparation and properties of other 3a*H*-indenes (**1**; R^1 ≠ methyl), with particular emphasis on the effect of the substituent R^1 on the rearrangement and cycloaddition reactions.



(**1**)

a; R^1 = R^2 = Me
b; R^1 = Me, R^2 = $SiMe_3$
c; R^1 = Et, R^2 = Me
d; R^1 = Pr^i, R^2 = $SiMe_2$
e; R^1 = CH_2Ph, R^2 = Me
f; R^1 = CH_2CH=CH_2, R^2 = Me
g; R^1 = CH_2C≡CH, R^2 = Me
h; R^1 = CH_2CO_2Me, R^2 = Me
i; R^1 = CH_2CO_2Me, R^2 = $SiMe_3$
j; R^1 = $CH_2CH_2OSiMe_3$, R^2 = $SiMe_3$

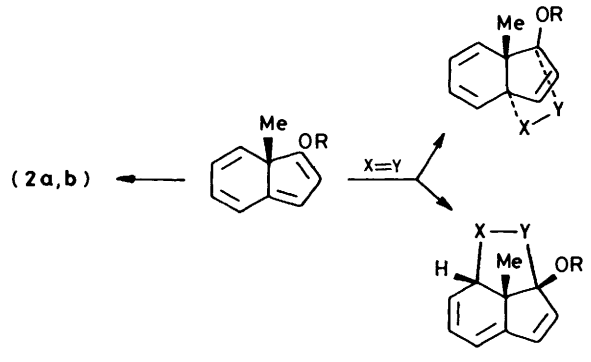


(**2**)

a; R^1 = R^2 = Me
b; R^1 = Me, R^2 = $SiMe_3$
c; R^1 = CH_2Ph, R^2 = Me
d; R^1 = CH_2CO_2Me, R^2 = Me

Results and Discussion

Reductive Alkylation of Indan-1-one.—The key step which introduces the substituent R^1 into the ring junction position involves the dissolving metal reduction of indan-1-one.[2,3,6] Although the use of alkylating agents other than iodomethane had not been studied in this system, a variety of electrophiles had been successfully used in the related reductive alkylation of acetophenone.[7] Based on our previous work,[3] indan-1-one and t-butyl alcohol were added to a solution of potassium in liquid ammonia. Addition of lithium bromide in tetrahydrofuran (THF), followed by quenching with the alkylating agent, gave the required tetrahydroindenones (**3**) in reasonable yield (Table 1). Several by-products analogous to those noted previously[3] were detected by t.l.c., although not isolated in every case. One unexpected by-product in the reaction involving prop-2-ynyl bromide was the triprop-2-ynyl derivative (**4**) in which all three positions α to the carbonyl group have been substituted. The initial product in the reductive alkylation using ethyl bromoacetate is the acid (**3f**), formed by *in situ* hydrolysis. This greatly facilitated the isolation of the product, and treatment of the acid (**3f**) with methanol–concentrated sulphuric acid gave the required ester (**3g**).

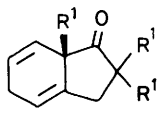


Scheme 1. R = Me, $SiMe_3$

A number of other alkylating agents were also employed in the reduction–alkylation sequence, but were found to be unsatisfactory. These included chloromethyl methyl ether, 2-iodoethanol and its tetrahydropyranyl ether, 2-iodomethyl-1,3-dioxolane, 2-bromo-1,1-diethoxyethane, epichlorohydrin, and

(3)

a; Et
b; Pr^i
c; $PhCH_2$
d; $H_2C{=}CHCH_2$
e; $HC{\equiv}CCH_2$
f; HO_2CCH_2
g; MeO_2CCH_2



(4)

$R^1 = CH_2C{\equiv}CH$

Table 1. Reductive alkylation of indan-1-one

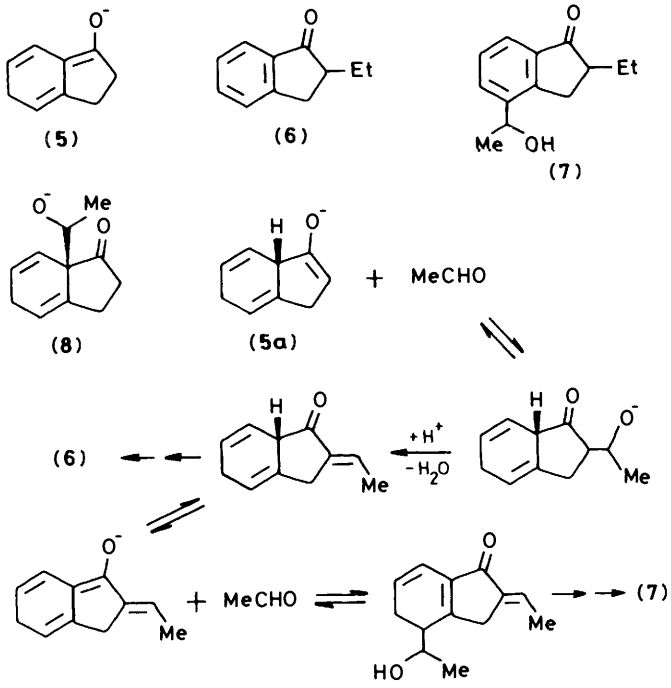
Compound	Alkylating Agent	% Yield
(**a**)	EtI	49
(**3b**)	Pr^iI	58
(**3c**)	$PhCH_2Br$	65
(**3d**)	$H_2C{=}CHCH_2Br$	60
(**3e**)	$HC{\equiv}CCH_2Br$	51
(**3f**)	EtO_2CCH_2Br	65
(**3g**)		90

ethylene oxide. Attempted conjugate addition of the intermediate enolate (**5**) to methyl acrylate also failed, but aldol condensation with acetaldehyde led, unexpectedly, to the aromatic compounds (**6**) (35%) and (**7**) (27%). Clearly the required addition to give compound (**8**) is readily reversible, and no products resulting from this intermediate were isolated. In contrast, if the enolate (**5a**), tautomeric with (**5**), adds to acetaldehyde there is the possibility of rapid and irreversible dehydration to form a conjugated enone, isomeric with product (**6**). This can aromatise to compound (**6**) or react further with acetaldehyde to give the alcohol (**7**); this sequence is summarised in Scheme 2.

Conversion of the Dienones (**3**) *into the Trienones* (**9**).—The best procedure for the introduction of the extra element of unsaturation involved α-phenylselenation of the ketone followed by oxidation of the selenide. The selenide could be prepared from the lithium enolate of the dienone, or from the trimethylsilyl enol ether (Scheme 3). Despite considerable effort the yields of the trienones (**9**) remained poor in most cases (Table 2), the problem lying in the selenation step. Occasionally

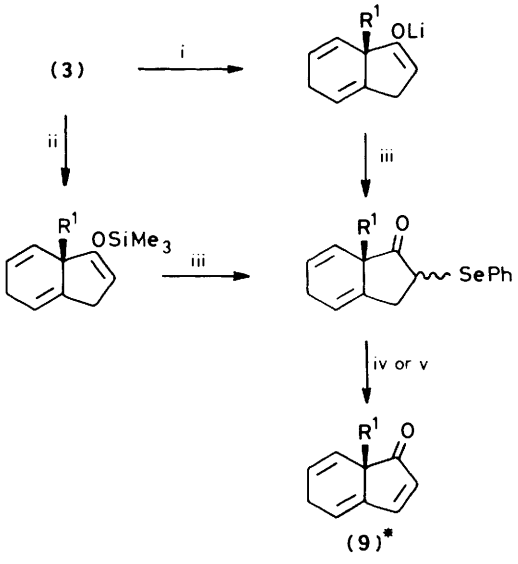
Table 2. Conversion of the dienones (**3**) into the trienones (**9**)

(**3**)/(**9**)	Method	% Yield
a	A	59
b	A	47
c	A	27
d	B	26
e	C	19
g	B	15
g	C	31



(5) (6) (7) (8) (5a)

Scheme 2.

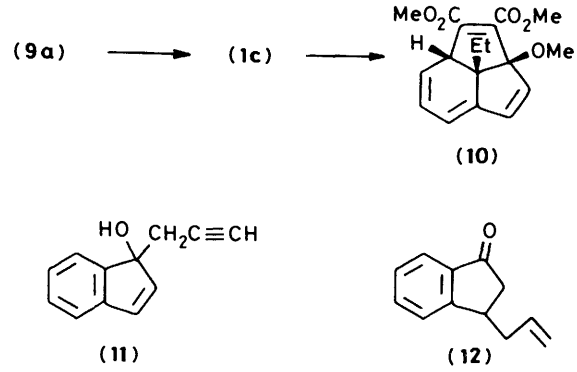


Method A: i, iii, iv
Method B: i, iii, v
Method C: ii, iii, v

* The substituents for (**9a**—**g**) are the same as for (**3a**—**g**).

Scheme 3. *Reagents*: i, $LiNPr^i_2$, THF, −78 °C; ii, Me_3SiCl, NaI, Et_3N, MeCN, 40 °C; iii, PhSeBr, THF, −78 °C; iv, H_2O_2, pyridine, 0 °C; v, *m*-CPBA, Et_2NH, THF, −10 °C

problems were encountered during the oxidation of the selenide. For example, the use of hydrogen peroxide in the allyl series (**3d**)—(**9d**) gave (*E*)-2-allylcinnamic acid (32%) as a by-product from a competing Baeyer–Villiger reaction, although this was suppressed by the use of 3-chloroperbenzoic acid (*m*-CPBA) as oxidant.



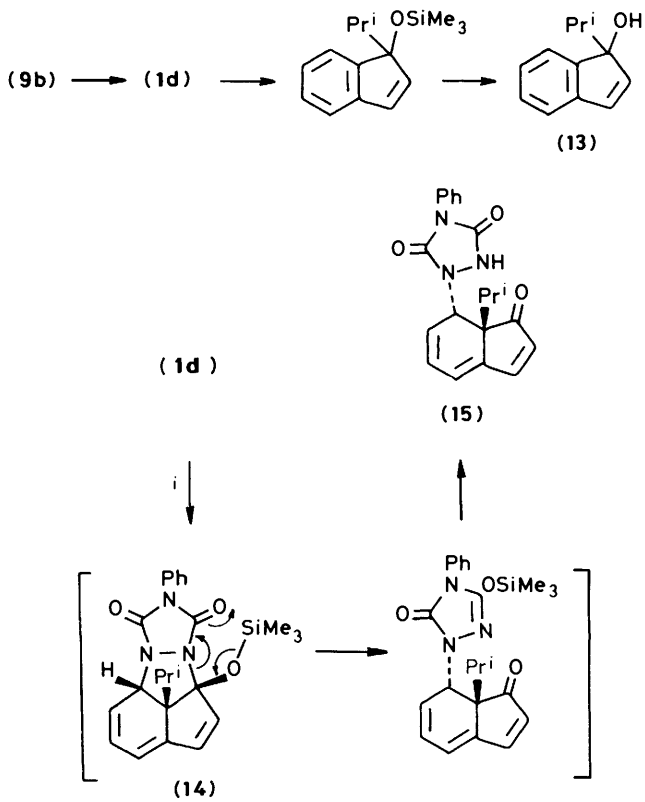
Preparation and Reactions of 3-*Methoxy*-3a-*substituted*-3a*H*-*indenes*.—The conversion of the trienone (**9a**) into the 3a*H*-indene (**1c**) proceeded as expected. Thus, deprotonation of the trienone (**9a**) with potassium hydride in 1,2-dimethoxyethane (DME) in the presence of 18-crown-6 gave a purple solution of the corresponding enolate. This was quenched by the addition of methyl fluorosulphonate to give a yellow solution of the 3a*H*-indene (**1c**), which underwent cycloaddition with dimethyl acetylenedicarboxylate (DMAD) to give the [8 + 2] cycloadduct (**10**) in 31% yield from compound (**9a**).

The reactions of trienones containing other substituents at the ring junction were less successful. 7a-Benzyl-5,7a-dihydro-1*H*-inden-1-one (**9c**) was converted into the 3a*H*-indene (**1e**) in the normal way, but failed to participate in cycloaddition with DMAD, or the more reactive 4-phenyl-1,2,4-triazole-3,5-dione (PTAD). The only product isolated was the 1*H*-isomer (**2c**). Similarly, enolisation of the trienone (**9g**) gave the rearranged indene (**2d**), the intermediate 3a*H*-indene (**1h**) not being intercepted by DMAD. Enolisation of the prop-2-ynyl derivative (**9e**) also resulted in rearrangement, and the 1*H*-isomer (**11**) was isolated, no methyl fluorosulphonate having been added in this case. Treatment of the allyl trienone (**9d**) under the standard conditions gave the indanone (**12**) (46%) as the only isolated product.

The fact that the benzyl-substituted 3a*H*-indene (**1e**) underwent rearrangement to the 1*H*-isomer so much more readily than the corresponding methyl and ethyl derivatives was somewhat surprising. However, studies on related 1*H*-indenes have shown that the relative rates of migration of methyl, ethyl, and benzyl groups in [1,5] shifts are 1:6.2:55.6.[8] The present study suggests that the CH_2CO_2Me and $CH_2C{\equiv}CH$ groups also migrate rapidly in sigmatropic rearrangements. In the case of the allyl derivative, the product (**12**) probably arises by a [3,3] sigmatropic rearrangement in the enolate formed by deprotonation of the trienone (**9d**).

Preparation and Reactions of 3a-*Substituted* 3-*trimethylsiloxy*-3a*H*-*indenes*.—The ready formation of 3a-methyl-3-trimethylsiloxy-3a*H*-indene (**1b**) from the corresponding trienone by treatment with chlorotrimethylsilane–sodium iodide–triethylamine in acetonitrile or with trimethylsilyl trifluoromethanesulphonate (TMS triflate) in ether in the presence of triethylamine,[3] prompted an investigation into the reaction of some of the trienones (**9**) with these silylating agents.

Addition of the isopropyl trienone (**9b**) to an acetonitrile solution of chlorotrimethylsilane, triethylamine, and sodium iodide at room temperature caused the appearance of a yellow colour, which was associated with the required 3a*H*-indene (**1d**). This colour gradually faded during 15 min, and subsequent treatment with fluoride ion and chromatography gave 1-isopropyl-1*H*-inden-1-ol (**13**) (79%). This rapid migration of the isopropyl group in (**1d**) at room temperature contrasts with the behaviour of the methyl-substituted 3a*H*-indene (**1b**) which rearranged rapidly only when heated to 80 °C, showing that isopropyl migrates more readily than methyl.



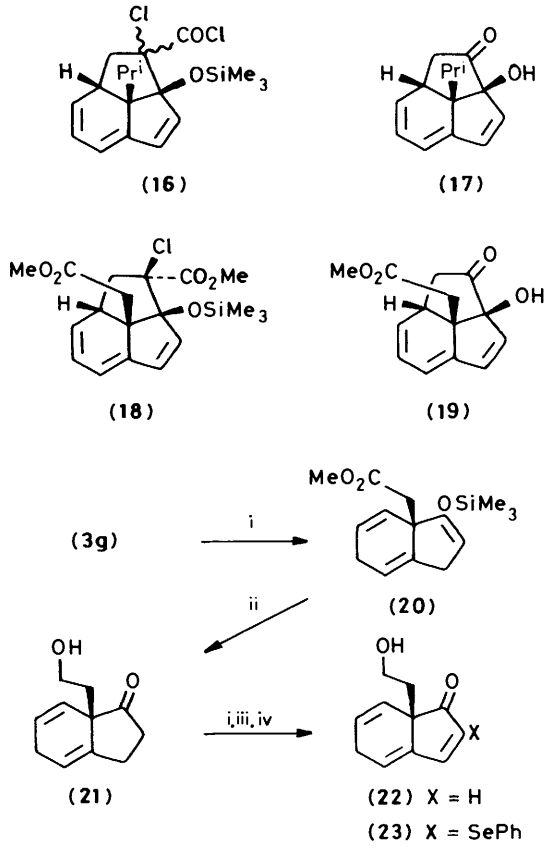
Scheme 4. *Reagents:* i, PTAD

The use of TMS triflate as the silylating agent allowed the 3a*H*-indene (**1d**) to be generated at −23 °C in THF. At this temperature, the indene could be intercepted with PTAD, although the initial cycloadduct (**14**) could not be isolated. After chromatography, the product was the trienone (**15**), possibly formed from the cyloadduct, as shown in Scheme 4.

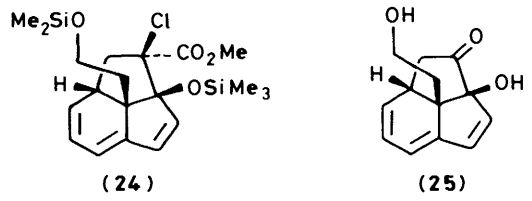
The 3a*H*-indene (**1d**) could also be intercepted by the ketene equivalent 2-chloroacryloyl chloride.[9] Thus generation of compound (**1d**) in DME at −23 °C with TMS triflate, was followed by the addition of 2-chloroacryloyl chloride. No attempt was made to isolate the initial adduct (**16**), which was treated directly with sodium azide, followed by warming to effect the Curtius rearrangement, and hydrolysis in aqueous acetic acid.[9] Chromatography of the mixture gave the rearranged indene (**13**) as the major product (44%), together with a small amount of the required tricyclic ketone (**17**). The poor yield of the cycloadduct compared with the corresponding methyl derivative is again attributed to the increased migratory aptitude of the isopropyl group.

The reaction of the trienone (**9g**) with TMS triflate in 1,2-dichloroethane, a solvent that is reported to increase the reactivity of the reagent,[10] at −23 °C allowed the generation of the 3a*H*-indene (**1i**). The addition of 2-chloroacryloyl chloride, followed by quenching of the reaction mixture with methanol–triethylamine, gave the cycloadduct (**18**) (15%). A similar sequence of reactions, but using DME as solvent, gave the adduct (**18**) in slightly higher yield (33%). The regiochemistry of the adduct (**18**) was deduced from its n.m.r. spectrum, and the stereochemistry was confirmed by *X*-ray crystallography.*

* Determined by Dr. D. J. Williams of this department.



Scheme 5. *Reagents:* i, Me_3SiCl, NaI, Et_3N, MeCN, 40 °C; ii, $LiAlH_4$, THF, 0 °C, then aq. work-up; iii, PhSeBr, THF, −78 °C; iv, *m*-CPBA, Et_2NH, THF, −10 °C



Attempts to quench the reaction mixture from the cycloaddition reaction with sodium azide under the standard conditions did not result in the formation of the required tricyclic ketone (**19**).

Failure to prepare the tricyclic ketone (**19**) from the trienone (**9g**) *via* the 3a*H*-indene (**1i**) prompted an investigation of an alternative trienone which contained the two-carbon ring junction substituent at a lower oxidation level, namely the 2-hydroxyethyl trienone (**22**). Although the precursor dienone (**21**) could not be prepared directly in the reductive alkylation of indan-1-one, it was readily prepared from the dienone (**3g**) (Scheme 5). Subsequent introduction of the extra double bond gave the required trienone (**22**) (22%) together with rather more of the selenated trienone (**23**) (28%). The trienone (**22**) was converted into the 3a*H*-indene (**1j**) by treatment with two equivalents of TMS triflate at −5 °C in DME. Although the 3a*H*-indene (**1j**) did not undergo cycloaddition with DMAD, it could be intercepted with 2-chloroacryloyl chloride and subsequently converted into the cycloadduct (**24**) (25%) by treatment with methanol. The stereochemistry of the adduct was not confirmed, but was assigned by analogy with that of the adduct (**18**). Treatment of the initial 2-chloroacryloyl chloride adduct with sodium azide under the standard conditions gave the required tricyclic ketone (**25**), although the overall yield from trienone (**22**) was low (11%).

Conclusions

Although cycloaddition to the methyl substituted 3a*H*-indenes (**1a**) and (**1b**) proceed well,[2,3] extension to other 3a*H*-indenes has met with only limited success. The increased migratory aptitude of the substituents employed compared with the methyl group means that rearrangement of the 3a*H*-indenes (**1**) to the 1*H*-isomers (**2**) occurs particularly easily, and prevents effective participation of the 3a*H*-indene in [8 + 2] cycloaddition reactions. Nevertheless, cycloadducts were obtained from the 3a*H*-indenes (**1c**), (**1d**), (**1i**), and (**1j**), albeit in low yield. The adducts (**10**) and (**17**) have subsequently been converted into tricyclic [10]annulenes.[11]

Experimental

For general points see refs. 3 and 5.

Reductive Alkylation of Indan-1-one.—General procedure. A mixture of indan-1-one (5.0 g, 0.038 mol) and t-butyl alcohol (6.28 g, 0.084 mol) in dry THF (50 ml) was added to a stirred solution of potassium (4.45 g, 0.114 g atom) in liquid ammonia (250 ml) at −78 °C. This addition was followed 30 min later by a solution of lithium bromide (8.67 g, 0.1 mol) in THF (50 ml). After a further 30 min, a mixture of water (40 ml), THF (40 ml), and the alkylating agent (Table 1) (0.041 mol) was added rapidly. The external cooling bath was removed, and the ammonia allowed to evaporate overnight. The residue was diluted with water (400 ml) and extracted with ether (3 × 300 ml). The combined extracts were dried, evaporated, and purified by chromatography. The following compounds were prepared. 7a-*Ethyl*-2,3,5,7a-*tetrahydro*-1H-*inden*-1-*one* (**3a**) (49%), b.p. 85 °C/3 mmHg; $\nu_{max.}$ 1 740 and 1 690 cm^{-1}; δ (250 MHz) 0.80 (3 H, t), 1.32—1.62 (2 H, qq), 2.12—2.30 (1 H, m), 2.45—2.68 (5 H, m), 5.78—5.86 (2 H, m), and 5.93 (1 H, m); *m/z* 162 (M^+), 133, 105, and 91; 2,4-*dinitrophenylhydrazone*, orange needles, m.p. 143—145 °C (Found: C, 59.5; H, 5.3; N, 16.25. $C_{17}H_{18}N_4O_4$ requires C, 59.6; H, 5.3; N, 16.4%).

7a-*Isopropyl*-2,3,5,7a-*tetrahydro*-1H-*inden*-1-*one* (**3b**) (58%), oil, $\nu_{max.}$ 1 740 cm^{-1}; δ (250 MHz; $CDCl_3$) 0.80 (3 H, d), 0.90 (3 H, d), 1.89 (1 H, m), 2.06—2.23 (1 H, m), 2.40—2.68 (5 H, m), 5.76—5.82 (1 H, m), 5.85 (1 H, br), and 5.89—5.97 (1 H, m); *m/z* 176 (M^+), 143, 142, 129, and 104; 2,4-*dinitrophenylhydrazone*, orange crystals, m.p. 172—173 °C (Found; C, 60.7; H, 5.6; N, 15.6. $C_{18}H_{20}N_4O_4$ requires C, 60.7; H, 5.7; N, 15.7%).

7a-*Benzyl*-2,3,5,7a-*tetrahydro*-1H-*inden*-1-*one* (**3c**) (65%), b.p. 114 °C/ 0.25 mmHg, m.p. 33—34 °C (Found: C, 85.6; H, 7.25. $C_{16}H_{16}O$ requires C, 85.7; H, 7.2%); $\nu_{max.}$ 1 740 and 1 695 cm^{-1}; δ (250 MHz; $CDCl_3$) 2.10—2.37 (3 H, m), 2.48 (1 H, dd, *J* 3.8, 7.1 Hz), 2.56 (1 H, d, *J* 12.9 Hz), 2.56 (3 H, m), 2.80 (1 H, d, *J* 12.9 Hz), 5.70 (1 H, br), 5.73—5.81 (1 H, m), 5.90 (1 H, dd, *J* 9.4, 2.8 Hz), and 7.0—7.25 (5 H, m); *m/z* 224 (M^+), 167, 165, and 133.

7a-*Allyl*-2,3,5,7a-*tetrahydro*-1H-*inden*-1-*one* (**3d**) (60%), oil, $\nu_{max.}$ 1 740 and 1 640 cm^{-1}; δ (250 MHz; $CDCl_3$) 2.07—2.30 (3 H, m), 2.40—2.75 (5 H, m), 4.96—5.08 (2 H, m), 5.55—5.75 (1 H, m), 5.78—5.83 (1 H, m), and 5.85—5.95 (2 H, m); *m/z* 174 (M^+), 157, 133, 132, and 105.

7a-*Prop*-2-*ynyl*-2,3,5,7a-*tetrahydro*-1H-*inden*-1-*one* (**3e**) (51%), oil, $\nu_{max.}$ 3 300 and 1 740 cm^{-1}; δ (90 MHz; $CDCl_3$) 1.95 (1 H, t), 1.95—3.00 (8 H, m), and 5.80—6.00 (3 H, m); *m/z* 132 and 104 (no M^+ observed). The reductive alkylation also gave 2,2,7a-*triprop*-2-*ynyl*-2,3,5,7a-*tetrahydro*-1H-*inden*-1-*one* (**4**) (8%), m.p. 77—80 °C (Found: C, 86.8; H, 6.6. $C_{18}H_{16}O$ requires C, 87.1; H, 6.5%); $\nu_{max.}$ 3 280, 3 260, 1 740, and 1 165 cm^{-1}; δ (250 MHz;

$CDCl_3$) 1.90 (1 H, t, *J* 2.5 Hz), 2.03—2.09 (2 H, m), 2.14 (1 H, dd, *J* 2.5, 1.2 Hz), 2.22 (1 H, d), 2.29 (1 H, t, *J* 2.5 Hz), 2.37 (1 H, d), 2.58—2.73 (4 H, m), 2.78—2.95 (1 H, m), 3.03—3.15 (1 H, m), 5.90 (1 H, dd, *J* 9.4, 2.5 Hz), and 5.98—6.10 (2 H, m); *m/z* 248 (M^+).

(1-*Oxo*-2,3,5,7a-*tetrahydro*-1H-*inden*-7a-*yl*)*acetic acid* (**3f**) (65%), b.p. 150 °C/0.15 mmHg, $\nu_{max.}$ 3 650—2 300, 1 740, and 1 705 cm^{-1}; δ (250 MHz; $CDCl_3$) 2.42 (1 H, d, *J* 14.4 Hz), 2.56 (1 H, d, *J* 14.4 Hz), 2.50—2.80 (6 H, m), 5.85—6.05 (3 H, m), and 9.8—10.6 (1 H, br); *m/z* 192 (M^+), 174, 133, 132, 131, 104, 103, and 102.

Methyl(1-*oxo*-2,3,5,7a-*tetrahydro*-1H-*inden*-7a-*yl*)*acetate* (**3g**). This was prepared (90%) by esterification of the above acid in methanol–concentrated sulphuric acid, $\nu_{max.}$ 1 735 cm^{-1}; δ (90 MHz; $CDCl_3$) 2.15—2.75 (8 H, m), 3.56 (3 H, s), and 5.75—5.95 (3 H, m); 2,4-*dinitrophenylhydrazone*, orange crystals, m.p. 163—165 °C (Found: C, 55.8; H, 4.7; N, 14.4. $C_{18}H_{18}N_4O_6$ requires C, 56.0; H, 4.7; N, 14.5%).

Dissolving Metal Reduction of Indan-1-one Followed by Addition of Acetaldehyde.—The reduction mixture (exactly as described in the general procedure) was quenched with acetaldehyde (1.84 g, 0.042 mol). Work-up and chromatography gave (i) 2-ethylindan-1-one (**6**) (2.12 g, 35%), b.p. 100 °C/0.15 mmHg (Kugelrohr) (lit.,[12] 65.5—67 °C/0.05 mmHg), and (ii) 2-*ethyl*-4-(1-*hydroxyethyl*)*indan*-1-*one* (**7**) (2.09 g, 27%), yellow oil, $\nu_{max.}$ 3 640—3 100, 1 700, 1 605, and 1 590 cm^{-1}; δ (250 MHz; $CDCl_3$) 0.96 (3 H, t), 1.38—1.55 (1 H, m), 1.52 (3 H, 2d), 1.86—1.98 (1 H, m), 2.44—2.60 (1 H, m), 2.75 (1 H, dq), 3.30 (1 H, dq), 3.40—3.60 (1 H, br), 5.05—5.20 (1 H, m), 7.34 (1 H, t), 7.59 (1 H, d), and 7.71 (1 H, d); *m/z* 204 (M^+). Oxidation of this alcohol with Jones reagent gave 4-*acetyl*-2-*ethylindan*-1-*one*, m.p. 59—62 °C (Found: C, 77.1; H, 7.0. $C_{13}H_{14}O_2$ requires C, 77.2; H. 7.0%).

Conversion of the Dienones (**3**) *into the Trienones* (**9**).—*Method A.* A solution of the dienone (**3**) (0.031 mol) in dry THF (30 ml) was added dropwise to a stirred solution of lithium di-isopropylamide [prepared from di-isopropylamine (5.32 ml, 0.038 mol) in THF (50 ml) and n-butyl-lithium (1.6 M; 23.8 ml, 0.038 mol)] at −78 °C under nitrogen. After 30 min, the solution was cooled to −90 °C and treated with a solution of phenylselenium bromide [from diphenyl diselenide (6.86 g, 0.022 mol) and bromine (3.52 g, 0.022 mol)] in THF (40 ml). The mixture was warmed to 0 °C during 30 min, poured into dilute hydrochloric acid, and extracted with ether. The combined ether extracts were dried and evaporated. The crude selenide was dissolved in THF (80 ml) and cooled to 0 °C. Pyridine (5 ml) was added followed by hydrogen peroxide dropwise (30%; 17 ml, 0.15 mol) maintaining the reaction temperature below 5 °C. The resulting mixture was poured into water, and extracted with ether (3 × 150 ml). The combined extracts were dried, evaporated, and the residue purified by chromatography. The following compounds were prepared by this method. 5,7a-*Dihydro*-7a-*ethyl*-1H-*inden*-1-*one* (**9a**) (59%), $\nu_{max.}$ 1 705 cm^{-1}; δ (250 MHz; $CDCl_3$) 0.85 (3 H, t), 1.45—1.75 (2 H, qq), 2.80—3.00 (2 H, m), 5.89—6.10 (3 H, m), 6.10 (1 H, dd, *J* 9.1, 2.5 Hz), and 7.69 (1 H, d, *J* 6.0 Hz); *m/z* 160 (M^+).

5,7a-*Dihydro*-7a-*isopropyl*-1H-*inden*-1-*one* (**9b**) (47%), $\nu_{max.}$ 1 705 cm^{-1}; δ (250 MHz; $CDCl_3$) 0.85 (6 H, 2 × d), 1.86 (1 H, m), 2.75—2.85 (2 H, m), 5.90 (1 H, d, *J* 6.0 Hz), 5.90—6.05 (2 H, m), 6.05 (1 H, dd, *J* 9.5, 2.5 Hz), and 7.69 (1 H, d, *J* 6.0 Hz); *m/z* 174 (M^+).

7a-*Benzyl*-5,7a-*dihydro*-1H-*inden*-1-*one* (**9c**) (27%), $\nu_{max.}$ 1 700 cm^{-1}; δ (60 MHz; $CDCl_3$) 2.2—2.65 (2 H, m), 2.88 (1 H, d, *J* 12 Hz), 3.06 (1 H, d, *J* Hz), 5.8—6.1 (3 H, m), 6.2 (1 H, dd), 7.0—7.5 (5 H, m), and 7.7 (1 H, d); *m/z* 222 (M^+), 131, 103, 102, 92, and 91.

Attempted Preparation of the Trienone (**9d**).—Treatment of the dienone (**3d**) (1.02 g, 5.86 mmol) as described above gave only (*E*)-3-[2-(*propen*-2-*yl*)*phenyl*]*propenoic acid* (0.35 g, 32%), m.p. 140—142 °C (Found: C, 76.6; H, 6.6. $C_{12}H_{12}O_2$ requires C, 76.6; H, 6.4%); $\nu_{max.}$ 3 400—2 300, 1 695, and 1 630 cm^{-1}; δ (250 MHz; $CDCl_3$), 3.54 (2 H, d), 4.99 (1 H, dd, *J* 17.0, 1.7 Hz), 5.10 (1 H, dd, *J* 10.0, 1.7 Hz), 5.88—6.06 (1 H, m), 6.38 (1 H, d, *J* 16.0 Hz), 7.15—7.40 (3 H, m), 7.62 (1 H, d), 8.10 (1 H, d, *J* 16..0 Hz), and 11.4 (1 H, br); *m/z* 188 (M^+), 143, 128, 116, and 115.

Method B. This was exactly the same as method A up to the isolation of the selenide. The crude selenide (from 0.031 mol of dienone) was dissolved in THF (75 ml) and cooled to −10 °C. *m*-Chloroperbenzoic acid (85%; 6.96 g) was added in portions so as to maintain the temperature at −10 °C. After 25 min, diethylamine (5 ml) was added and the mixture allowed to warm up to room temperature. The mixture was poured into water (100 ml) and extracted with ether (3 × 100 ml). The combined ether extracts were washed with saturated sodium hydrogen carbonate, dried, evaporated, and chromatographed. The following compounds were prepared by this method. 7a-*Allyl*-5,7a-*dihydro*-1H-*inden*-1-*one* (**9d**) (26%), $\nu_{max.}$ 1 705 cm^{-1}; δ (60 MHz; $CDCl_3$) 2.15—2.40 (2 H, m), 2.70—2.85 (2 H, m), 4.75—5.10 (2 H, m), 5.5—6.1 (5 H, m), and 7.58 (1 H, d, *J* 6.0 Hz), *m/z* 172 (M^+), 131, 130, 103, and 102.

Methyl(1-*oxo*-5,7a-*dihydro*-1H-*inden*-7a-*yl*)*acetate* (**9g**) (15%), $\nu_{max.}$ 1 745 and 1 705 cm^{-1}; δ (250 MHz; $CDCl_3$) 2.51 (2 H, ABq, *J* 12.5 Hz), 2.84—2.92 (2 H, m), 3.60 (3 H, s), 5.93—6.03 (1 H, m), 6.00 (1 H, d, *J* 5.8 Hz), 6.12—6.17 (1 H, m), 6.15 (1 H, dd, *J* 9.2, 2.5 Hz), and 7.74 (1 H, d, *J* 5.8 Hz); *m/z* 204 (M^+), 177, 176, 131, and 117.

Method C. Chlorotrimethylsilane (3.08 ml, 0.024 mol) was added to a stirred solution of sodium iodide (3.64 g, 0.024 mol) in acetonitrile (40 ml) at room temperature. After 5 min, a solution of the dienone (**3**) (0.019 mol) and triethylamine (3.37 ml, 0.024 mol) in acetonitrile (20 ml) was added. After 1.5 h, the mixture was extracted with light petroleum (5 × 50 ml); the light petroleum extracts were evaporated and the residue dissolved in THF (100 ml). This solution was cooled to −90 °C and treated dropwise with a solution of phenylselenium bromide [from diphenyl diselenide (2.96 g, 9.5 mmol) and bromine (1.52 g, 9.5 mmol)] in THF (30 ml). The mixture was warmed to room temperature, worked-up, and the crude selenide treated as described under method B. The following compounds were prepared by this method. 7-*Prop*-2-*ynyl*-5,7a-*dihydro*-1H-*inden*-1-*one* (**9e**) (19%), $\nu_{max.}$ 3 290 and 1 700 cm^{-1}; δ (90 MHz; $CDCl_3$) 1.80 (1 H, t, *J* 2 Hz), 2.25 (2 H, m), 2.6—2.8 (2 H, m), 5.8—6.1 (4 H, m), and 7.60 (1 H, d, *J* 5 Hz); *m/z* 170 (M^+), 141, 131, 115, and 103.

Methyl (1-oxo-5,7a-dihydro-1H-inden-7a-yl)acetate (**9g**) (31%); data already given.

Preparation and Reactions of 3-*Methoxy*-3a-*substituted*-3aH-*indenes. General Procedure.*—A solution of 18-crown-6 (0.83 g, 3.1 mmol) in dry DME (5 ml) was added to a stirred suspension of potassium hydride (25%; 0.18 g, 4.5 mmol) and dry DME (20 ml) at −23 °C under nitrogen. This was followed by the addition of the trienone (3.1 mmol) in DME (5 ml) and, 5 min later, by methyl fluorosulphonate (0.27 ml, 3.3 mmol) (**CAUTION: HIGHLY TOXIC**). The resulting solution was stirred a further 5 min, then treated with a solution of dimethyl acetylenedicarboxylate (0.48 g, 3.4 mmol) in DME (5 ml), and the mixture allowed to warm to room temperature during 2 h. Triethylamine was added, the mixture filtered through Celite, and the filtrate evaporated, and purified by chromatography.

Dimethyl 7b-*ethyl*-2a-*methoxy*-7a,7b-*dihydro*-2aH-*cyclopent*-[cd]*indene*-1,2-*dicarboxylate* (**10**). The trienone (**9a**) (2.48 g, 15.5 mmol) was treated as described above and gave the *title compound* (**10**) (1.50 g, 31%), m.p. 74—76 °C (from light

petroleum) (Found: C, 68.4; H, 6.35. $C_{18}H_{20}O_5$ requires C, 68.3; H, 6.4%); $\nu_{max.}$ 1 735 and 1 700 cm^{-1}; δ (250 MHz; $CDCl_3$) 0.87 (3 H, t), 1.35—1.65 (2 H, qq), 3.39 (3 H, s), 3.78 (3 H, s), 3.79 (3 H, s), 5.83 (1 H, dd, *J* 8.2, 5.6 Hz), 5.96 (1 H, d, *J* 5.3 Hz), 6.09 (1 H, ddd, *J* 8.2, 5.3, 1.9 Hz), 6.38 (1 H, d, *J* 5.6 Hz), and 6.50 (1 H, d, *J* 5.6 Hz); *m/z* 316 (M^+).

Use of the trienone (**9c**). The trienone (**9c**) (0.70 g) was treated as described above and gave 1-*benzyl*-1-*methoxy*-1H-*indene* (**2c**) (424 mg, 57%), b.p. 125 °C/0.2 mmHg (Kugelrohr) (Found: C, 86.5; H, 6.9. $C_{17}H_{16}O$ requires C, 86.4; H, 6.8%); δ (250 MHz; $CDCl_3$) 2.94 (3 H, s), 2.98 (1 H, d, *J* 12.5 Hz), 3.24 (1 H, d, *J* 12.5 Hz), 6.10 (1 H, d, *J* 5.8 Hz), 6.61 (1 H, d, *J* 5.8 Hz), and 7.05—7.25 (9 H, m); *m/z* 236 (M^+), 145, 130, 115, 102, and 91.

Use of the trienone (**9g**). The trienone (**9g**) (270 mg) was treated as described above and gave *methyl* (1-*methoxy*-1H-*inden*-1-*yl*)*acetate* (**2d**) (70 mg, 24%), $\nu_{max.}$ 1 735 cm^{-1}; δ (90 MHz; $CDCl_3$) 2.49 (1 H, d, *J* 14 Hz), 2.95 (3 H, s), 3.10 (1 H, d, *J* 14 Hz), 3.70 (3 H, s), 6.61 (1 H, d, *J* 6 Hz), 6.82 (1 H, d, *J* 6 Hz), and 7.3 (5 H, m); *m/z* 218 (M^+). Hydrolysis of compound (**2d**) gave (1-*methoxy*-1H-*inden*-1-*yl*)*acetic acid*, m.p. 88—91 °C (Found: C, 70.5; H, 5.95. $C_{11}H_{10}O_3$ requires C, 70.6; H, 5.9%).

Use of the trienone (**9e**). The trienone (**9e**) (220 mg) was treated as described above except that two equivalents of base were used, and the reaction was quenched with methanol before the addition of the methyl fluorosulphonate. Work-up and chromatography gave 1-*prop*-2-*ynyl*-1H-*inden*-1-*ol* (**11**) (89 mg, 41%), m.p. 84—85 °C (Found: C, 84.5; H, 6.0. $C_{12}H_{10}O$ requires C, 84.7; H, 5.9%); $\nu_{max.}$ 3 600 and 3 310 cm^{-1}; δ (90 MHz; $CDCl_3$) 2.05 (1 H, t, *J* 2 Hz), 2.25—2.40 (1 H, br), 2.68 (2 H, dd, *J* 16, 2 Hz), 6.34 (1 H, d, *J* 5 Hz), 6.63 (1 H, d, *J* 5 Hz), and 7.1—7.5 (4 H, m); *m/z* 170 (M^+), 131, and 103.

Use of the trienone (**9d**). The trienone (**9d**) (270 mg) was treated as described above and gave 3-*allylindan*-1-*one* (**12**) (124 mg, 46%), b.p. 130 °C/0.25 mmHg (Kugelrohr) (Found: C, 83.5; H, 6.8. $C_{12}H_{12}O$ requires C, 83.6; H, 7.0%); $\nu_{max.}$ 1 700 cm^{-1}; δ (250 MHz; $CDCl_3$) 2.25—2.40 (1 H, m), 2.41 (1 H, dd, *J* 18.3, 3.3 Hz), 2.59—2.70 (1 H, m), 2.82 (1 H, dd, *J* 18.3, 7.5 Hz), 3.42—3.54 (1 H, m), 5.05—5.15 (2 H, m), 5.75 (1 H, qt, *J* 17.5, 10.0, 6.7 Hz), 7.38 (1 H, t), 7.50—7.65 (2 H, m), and 7.75 (1 H, d); *m/z* 172 (M^+), 132, 131, and 104.

Preparation and Reactions of 3a-*Substituted*-3-*trimethylsiloxy*-3aH-*indenes*.

Generation of the Isopropyl-3aH-*indene* (**1d**).—(*a*) *Using chlorotrimethylsilane, sodium iodide, and triethylamine.* Chlorotrimethylsilane (0.25 ml, 2.0 mmol) was added to a solution of sodium iodide (0.30 g, 2.0 mmol) in dry acetonitrile (10 ml). A mixture of the trienone (**9b**) (140 mg, 0.8 mmol) and triethylamine (0.20 g, 2.0 mmol) was added, and the resulting yellow solution stirred for 15 min at 20 °C. At the end of this period, the colour had faded. Aqueous work-up and treatment with potassium fluoride, and chromatography gave 1-*isopropyl*-1H-*inden*-1-*ol* (**13**) (110 mg, 79%), m.p. 51—52 °C (Found: C, 82.6; H, 8.1. $C_{12}H_{14}O$ requires C, 82.7; H, 8.1%); $\nu_{max.}$ 3 300br cm^{-1}; δ (250 MHz; $CDCl_3$) 0.67 (3 H, d), 1.08 (3 H, d), 2.0 (1 H, br), 2.26 (1 H, septet), 6.24 (1 H, d, *J* 5.2 Hz), 6.63 (1 H, d, *J* 5.2 Hz), and 7.10—7.32 (4 H, m); *m/z* 174 (M^+), 173, 159, and 131.

(*b*) *Using trimethylsilyl trifluoromethanesulphonate and triethylamine.* A solution of the trienone (**9b**) (200 mg, 1.15 mmol) in dry THF at —23 °C was treated with triethylamine (0.32 ml, 2.3 mmol). Trimethylsilyl trifluoromethanesulphonate (0.3 ml, 1.65 mmol) was added and the mixture stirred at −23 °C for 0.5 h. A solution of 4-phenyl-1,2,4-triazole-3,5-dione (220 mg, 1.26 mmol) in THF (5 ml) was added and the mixture stirred for a further 1 h at −23 °C before warming to room temperature. Work-up and chromatography gave 7-(3,5-*dioxo*-4-*phenyl*-1,2,4-*triazolin*-1-*yl*)-7a-*isopropyl*-7,7a-*dihydro*-1H-*inden*-1-*one* (**15**) (88 mg, 22%), m.p. 166—168 °C (Found: C, 68.5; H, 5.5; N, 12.0. $C_{20}H_{19}N_3O_3$ requires C, 68.75; H, 5.5; N, 12.0%); $\nu_{max.}$ 1 760 and 1 700 cm^{-1}; δ (250 MHz; $CDCl_3$) 0.86 (3 H, d), 1.04 (3 H, d), 2.02 (1 H, septet), 5.28 (1 H, d, *J* 5.6 Hz), 5.90 (1 H, dd, *J* 8.8, 5.6 Hz), 6.02 (1 H, d, *J* 5.0 Hz), 6.18 (1 H, d, *J* 5.6 Hz), 6.33 (1 H, dd, *J* 8.8, 5.0 Hz), 7.33—7.56 (5 H, m), and 7.62 (1 H, d, *J* 5.6 Hz).

Preparation of the Tricyclic Ketone (**17**).—A solution of the trienone (**9b**) (384 mg, 2.21 mmol) in dry DME (25 ml) was cooled to −23 °C, and treated with triethylamine (0.4 ml, 2.9 mmol) and then trimethylsilyl trifluoromethanesulphonate (0.48 ml, 2.64 mmol). After 1 h at −23 °C, a solution of 2-chloroacryloyl chloride (0.33 g, 2.66 mmol) in dry DME (5 ml) was added and the reaction mixture allowed to warm up to 0 °C during 45 min. Finely powdered sodium azide (1 g, 15.5 mmol) was added and stirring continued for 5.5 h at room temperature. The mixture was filtered, the filtrate refluxed for 2.75 h, treated with aqueous acetic acid (65%; 12 ml), and heated at 80 °C for a further 1 h. Potassium fluoride (500 mg) was added, and the mixture poured into water (60 ml). The products were extracted with ether (4 × 30 ml), and chromatographed to give (i) 1-isopropyl-1*H*-inden-1-ol (**13**) (171 mg, 44%) and (ii) 2a-*hydroxy*-7b-*isopropyl*-1,2a,7a,7b-*tetrahydro*-2H-*cyclopent*[cd]*inden*-2-*one* (**17**) (17 mg, 3.6%), $\nu_{max.}$ 3 540 and 1 740 cm^{-1}; δ (250 MHz; $CDCl_3$) 0.94 (3 H, d), 0.97 (3 H, d), 2.06 (1 H, septet), 2.35 (1 H, dd, *J* 11.9, 16.3 Hz), 2.51 (1 H, dd, *J* 16.3, 6.9 Hz), 2.68 (1 H, br), 2.94 (1 H, ddd, *J* 6.3, 6.9, 11.9 Hz), 5.82—5.92 (2 H, m), 5.88 (1 H, d, *J* 5.6 Hz), 5.99 (1 H, dd, *J* 9.1, 5.0 Hz), and 6.54 (1 H, d, *J* 5.6 Hz); *m/z* 216 (M^+), 174, 159, 145, and 131.

Preparation of the Tricyclic Adduct (**18**).—(*a*) The trienone (**9g**) (88 mg, 0.43 mmol) in 1,2-dichloroethane (10 ml) was treated with triethylamine (0.12 ml, 0.9 mmol) and trimethylsilyl trifluoromethanesulphonate (0.1 ml, 0.5 mmol) at −23 °C. 2-Chloroacryloyl chloride (0.15 ml) was added, and the mixture stirred at −23 °C for 10 min, then at 0 °C for 30 min. The mixture was treated with methanol (1 ml) and triethylamine (1 ml) for 1 h at room temperature, poured into water, and extracted with ether. The extracts were dried, evaporated, and chromatographed to give *methyl* (2aα,7aα,-7bβ)-2-*chloro*-7b-*methoxycarbonylmethyl*-2a-*trimethylsiloxy*-2,2a,7a,7b-*tetrahydro*-1H-*cyclopent*[cd]*indene*-2β-*carboxylate* (**18**) (24.8 mg, 15%), m.p. 91—93 °C (Found: C, 57.7; H, 6.4. $C_{19}H_{25}ClO_5Si$ requires C, 57.5; H, 6.3%); δ (250 MHz; $CDCl_3$) 0.19 (9 H, s), 2.05 (1 H, dd, *J* 13.8, 12.5 Hz), 2.19 (2 H, ABq, *J* 15.0 Hz), 2.26 (1 H, dd, *J* 13.8, 6.3 Hz), 3.55—3.75 (1 H, m), 3.60 (3 H, s), 3.72 (3 H, s), 5.88 (1 H, d, *J* 5.0 Hz), 5.96 (1 H, dd, *J* 9.4, 5.9 Hz), 6.00 (1 H, d, *J* 5.4 Hz), 6.08 (1 H, dd, *J* 9.4, 5.0 Hz), and 6.52 (1 H, d, *J* 5.4 Hz); *m/z* 398/396 (M^+), 276, and 203.

(*b*) A solution of the trienone (**9g**) (1.136 g, 5.6 mmol) in dry DME (20 ml) was cooled to −23 °C and treated with triethylamine (0.97 ml, 7.0 mmol) and trimethylsilyl trifluoromethanesulphonate (1.27 ml, 7.0 mmol) as described above. 2-Chloroacryloyl chloride was added and the mixture treated as above to give the adduct (**18**) (0.735 g, 33%).

7a-(2-*Hydroxyethyl*)-2,3,5,7a-*tetrahydro*-1H-*inden*-1-*one* (**21**).—Chlorotrimethylsilane (14.0 ml, 11 mmol) was added to a solution of sodium iodide (16.4 g, 11 mmol) in dry acetonitrile (150 ml). A solution of the dienone (**3g**) (19.0 g, 8.8 mmol) and triethylamine (15.3 ml, 11 mmol) was added, and the resulting mixture stirred at 40 °C for 1.5 h. The product was extracted with light petroleum (500 ml), and evaporated to give the silyl ether (**20**) (18.0 g, 70%) as an orange oil. The silyl ether (**20**) (7.14 g, 25 mmol) was dissolved in dry THF (50 ml) and added dropwise to a suspension of lithium aluminium hydride (3.80 g,

100 mmol) in THF at 0 °C. The mixture was stirred at room temperature for 2 h. Standard work-up and chromatography gave the title compound (**21**) (1.84 g, 40%), $\nu_{max.}$ 3 600—3 100 and 1 730 cm^{-1}; δ (250 MHz; $CDCl_3$) 1.50—2.30 (4 H, m), 2.52—2.85 (4 H, m), 3.40—3.57 (2 H, m), and 5.80—6.15 (3 H, m); *m/z* 178 (M^+), 117, 105, and 91.

7a-(2-*Hydroxyethyl*)-5,7a-*dihydro*-1H-*inden*-1-*one* (**22**).—Chlorotrimethylsilane (3.6 ml, 28.3 mmol) was added to a stirred solution of sodium iodide (4.3 g, 28.7 mmol) in acetonitrile. A solution of the dienone (**21**) (1.70 g, 9.6 mmol) and triethylamine (3.97 ml, 28.6 mmol) in acetonitrile (20 ml) was added, and the resulting mixture stirred at 40 °C for 2 h. The product was extracted with light petroleum (250 ml) and evaporated to give 3-*trimethylsiloxy*-3a-(2-*trimethylsiloxyethyl*)-3a,6-*dihydro*-1H-*indene* (3.01 g, 98%), δ (60 MHz; $CDCl_3$) 0.15 (9 H, s), 0.30 (9 H, s), 1.5—2.0 (2 H, m), 2.5—3.1 (4 H, m), 3.5—3.8 (2 H, m), 4.8 (1 H, m), and 5.8—6.1 (3 H, m). The selenation and subsequent oxidation of this compound was carried out as described earlier (method C) and gave after chromatography (i) 7a-(2-*hydroxyethyl*)-2-*phenylseleno*-5,7a-*dihydro*-1H-*inden*-1-*one* (**23**) (870 mg, 28%), $\nu_{max.}$ 3 650—3 100 and 1 705 cm^{-1}; δ (250 MHz; $CDCl_3$) 1.75—1.98 (2 H, m), 2.70—2.85 (2 H, m), 3.45—3.75 (2 H, m), 5.79 (1 H, t, *J* 4.5 Hz), 5.92 (1 H, m), 6.14 (1 H, d, *J* 9.0 Hz), 7.10 (1 H, s), and 7.30—7.64 (5 H, m); *m/z* 332/330 (M^+); attempted purification by distillation caused extensive decompostion, and (ii) 7a-(2-*hydroxyethyl*)-5,7a-*dihydro*-1H-*inden*-1-*one* (**22**) (367 mg, 22%), $\nu_{max.}$ 3 680—3 140 and 1 705 cm^{-1}; δ (250 MHz; $CDCl_3$) 1.75—1.93 (2 H, m), 2.86—2.93 (2 H, m), 3.57—3.81 (2 H, m), 5.93—6.00 (1 H, m), 6.03 (1 H, d, *J* 5.8 Hz), 6.08 (1 H, t, *J* 4.5 Hz), 6.19 (1 H, d, *J* 9.0 Hz), and 7.72 (1 H, d, *J* 5.8 Hz); *m/z* 176 (M^+) and 131; attempted purification by distillation caused decomposition.

Preparation of the Tricyclic Adduct (**24**).—A solution of the trienone (**22**) (127 mg, 0.72 mmol) in dry DME (15 ml) at 0 °C was treated with triethylamine (0.25 ml, 1.8 mmol) and trimethylsilyl trifluoromethanesulphonate (0.33 ml, 1.8 mmol). The mixture was stirred for 1 h at 0 °C, and then 2-chloroacryloyl chloride (0.2 ml) was added. After a further 1 h at 0 °C, methanol (2 ml) and triethylamine (1 ml) were added. Aqueous work-up and chromatography gave the adduct *methyl* (2aα,7aα,-7bβ)-2-*chloro*-2a-*trimethylsiloxy*-7b-(2-*trimethylsiloxyethyl*)-2,2a,7a,7b-*tetrahydro*-1H-*cyclopent*[cd]*indene*-2β-*carboxylate* (**24**) (78 mg, 25%), b.p. 120 °C/0.2 mmHg (Kugelrohr) (Found: C, 57.1; H, 7.6; Cl, 7.9. $C_{21}H_{33}ClO_4Si_2$ requires C, 57.0; H, 7.75; Cl, 8.0%); $\nu_{max.}$ 1 742 cm^{-1}; δ (250 MHz; CDCl) 0.08 (9 H, s), 0.21 (9 H, s), 1.39—1.51 (1 H, ddd, *J* 6.9, 7.5, 14.4 Hz), 1.64—1.76 (1 H, ddd, *J* 5.6, 7.5, 14.4 Hz), 2.01 (1 H, dd, *J* 12.5, 13.8 Hz), 2.19 (1 H, dd, *J* 13.8, 5.0 Hz), 2.96 (1 H, ddd, *J* 5.0, 5.6, 12.5 Hz), 3.63 (2 H, 2 × t, *J* 7.5, 6.9 Hz), 3.74 (3 H, s), 5.81 (1 H, d, *J* 4.9 Hz), 5.91 (1 H, dd, *J* 5.6, 9.2 Hz), 5.92 (1 H, d, *J* 5.7 Hz), 6.06 (1 H, dd, *J* 5.6, 9.2 Hz), and 6.47 (1 H, d, *J* 5.7 Hz); *m/z* 442/440 (M^+), 320, 230, 217, and 203.

Preparation of the Tricyclic Ketone (**25**).—A solution of the 3a*H*-indene (**1j**) [prepared from the trienone (**22**) (114 mg, 0.65 mmol)] was treated with 2-chloroacryloyl chloride (0.18 ml). The initial adduct was treated with sodium azide as described previously for compound (**17**). Subsequent work-up as before and chromatography gave 2a-*hydroxy*-7b-(2-*hydroxyethyl*)-1,2a,7a,7b-*tetrahydro*-2H-*cyclopent*[cd]*inden*-2-*one* (**25**) (15 mg, 11%), $\nu_{max.}$ 3 460 and 1 745 cm^{-1}; δ (250 MHz; $CDCl_3$) 1.75—1.88 (1 H, m), 2.21—2.29 (1 H, m), 2.37 (1 H, dd, *J* 12.6, 17.1 Hz), 2.57 (1 H, dd, *J* 6.9, 17.1 Hz), 2.72—2.80 (1 H, m), 4.05—4.12 (2 H, m), 5.88 (1 H, dd, *J* 6.0, 9.3 Hz), 5.98 (1 H, d, *J* 5.1 Hz), 6.09—6.15 (2 H, m), and 6.45 (1 H, d, *J* 5.1 Hz); *m/z* 216 (M − 2), 200, 172, 171, and 130.

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