3a*H*-Indenes. Part 6.[1] Cycloaddition of 3-Methoxy- and 3-Trimethylsiloxy-3a-methyl-3a*H*-indenes to Heterodienophiles; Approaches to Aza[10]annulenes

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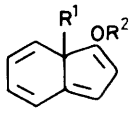
3-Methoxy-3a-methyl-3a*H*-indene (**4a**) reacts with dimethyl azodicarboxylate and with bistrichloroethyl azodicarboxylate to give the [8 + 2]-cycloadducts (**5a**) and (**5c**), respectively. 3-Trimethylsiloxy-3a-methyl-3a*H*-indene (**4b**) reacts similarly with the same two azo esters to give cycloadducts (**5b**) and (**5d**) which, on isolation, give the ring-opened ketones (**6a**) and (**6b**). Reduction of the bistrichloroethyl ester (**5c**) with zinc followed by oxidation with copper(II) chloride regenerates the 3a-methylindene (**4a**); the proposed pathway for this is shown in Scheme 2. The 3a-trimethylsiloxyindene (**4b**) undergoes [8 + 2]-cycloaddition to trichloroacetonitrile to give the adduct (**10**) which is hydrolysed by acid to the diketone (**11**). 3a-Methylindene (**4a**) reacts with toluene-*p*-sulphonyl isocyanate to give the cycloadduct (**12**) and with chlorosulphonyl isocyanate to give, after hydrolysis, the [8 + 2]-cycloadducts (**13**) and (**14**) which are converted by methyl fluorosulphonate into the cyclic imidates (**16**) and (**17**) respectively. Attempts to transform these various [8 + 2]-adducts into mono-aza and di-aza analogues of 7b-methyl-7b*H*-cyclopent[*cd*]indene were unsuccessful.

In previous papers[1,2,3] we have described the preparation and reactions of the 3a*H*-indene ring system (**1**). These bicyclic conjugated polyenes are isolable but reactive species which readily rearrange and which participate in cycloaddition reactions with a range of olefinic and acetylenic 2π-components. We have now investigated the reactions of 3a-methyl-3a*H*-indenes with heterodienophiles as an approach to the synthesis of aza analogues of tricyclic [10]annulenes, and we report on the cycloaddition of these reactive polyenes to N=N, C≡N, and C=N bonds.

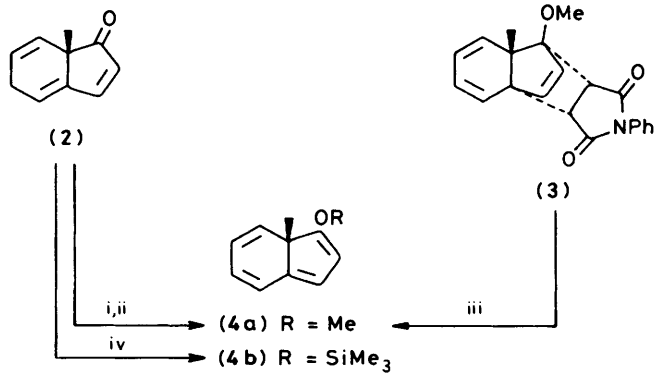


(**1**)

R^1 = various alkyl groups
R^2 = Me or $SiMe_3$

Results and Discussion

3-Methoxy-3a-methyl-3a*H*-indene (**4a**) was prepared from the trienone (**2**) by deprotonation followed by methylation of the extended enolate as previously described,[2,3] although in certain cases (see below) it was more convenient to use the *N*-phenylmaleimide adduct (**3**) as a source of (**4a**). The adduct (**3**) undergoes a retro [4 + 2]cycloaddition on heating in toluene.[2] The 3-trimethylsiloxyindene (**4b**) was also prepared from the trienone (**2**) by treatment with trimethylsilyl trifluoromethanesulphonate and triethylamine[2] (Scheme 1).



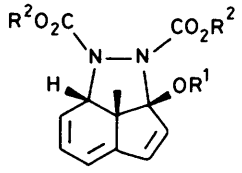
Scheme 1. *Reagents:* i, KH, 18-crown-6, 1,2-dimethoxyethane, −23 °C; ii, $MeOSO_2F$; iii, toluene, heat; iv, $Me_3SiOSO_2CF_3$, Et_3N, Et_2O

Addition to N=N *Bonds.*—Azo compounds in which the azo bond is flanked by two carbonyl functions are highly reactive, and many examples of cycloaddition to the N=N bond are known.[4] Indeed the cyclic azo dienophile, 4-phenyl-1,2,4-triazole-3,5-dione, reacts extremely rapidly with 3-methoxy-3a-methyl-3a*H*-indene (**4a**).[3] Encouraged by this result, we investigated the reactions of the 3a*H*-indenes (**4a**) and (**4b**) with other azo dienophiles.

Although initial attempts to effect the cycloaddition of the 3a*H*-indene (**4a**) with diethyl azodicarboxylate were disappointing,[3] use of the more reactive[5] dimethyl azodicarboxylate was more successful. Thus addition of excess of the azo dienophile to a solution of the 3a*H*-indene (**4a**) in 1,2-dimethoxyethane gave a 49% yield of the crystalline [8 + 2]-adduct (**5a**). Use of the trimethylsiloxy-3a*H*-indene (**4b**) gave the corresponding cycloadduct (**5b**) in low yield which on treatment with fluoride ion during work-up gave the ketone (**6a**), where cleavage of the O–Si bond is accompanied by opening of the heterocyclic ring. The ketone (**6a**) could also be obtained in high yield by treatment of the methoxy adduct (**5a**) with aqueous sulphuric acid. Attempts to cleave the ester groups in adduct (**5a**) by alkaline hydrolysis were unsuccessful.

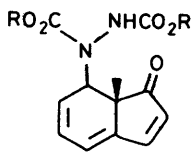
Bistrichloroethyl azodicarboxylate[6] also underwent cycloaddition to the 3a*H*-indenes (**4**). Although the [8 + 2]-adduct (**5c**) was only obtained in poor yield when the 3a*H*-indene (**4a**) was prepared from the trienone (**2**), the yield of adduct was increased to 63% when the 3a*H*-indene (**4a**) was generated thermally from the *N*-phenylmaleimide adduct (**3**). The ^1H n.m.r. spectrum of the adduct (**5c**) showed considerable temperature dependence, with all the signals being broadened at ambient temperature. At 90 °C the resonances attributed to the methylene protons of the two urethane groups were resolved into two AB systems. The corresponding [8 + 2]-adduct (**5d**) derived from the trimethylsiloxy-3a*H*-indene (**4b**) could not be

isolated, and underwent hydrolysis and ring opening to the ketone (**6b**) during aqueous work-up.



(5)

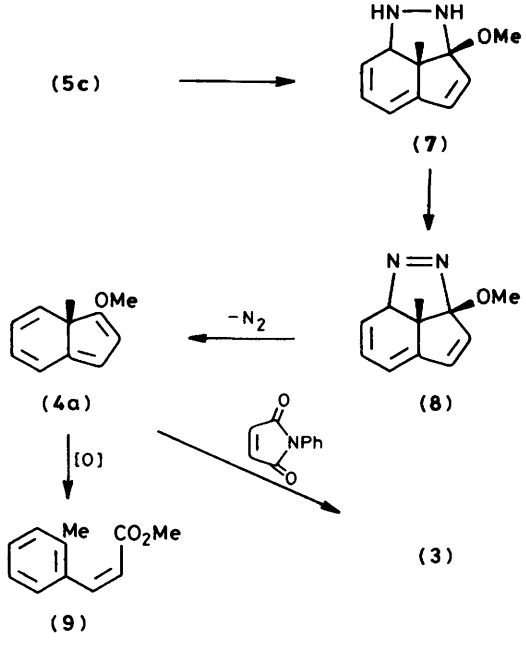
a; $R^1 = R^2 = Me$
b; $R^1 = SiMe_3$, $R^2 = Me$
c; $R^1 = Me$, $R^2 = CH_2CCl_3$
d; $R^1 = SiMe_3$, $R^2 = CH_2CCl_3$



(6)

a; R = Me
b; R = CH_2CCl_3

Conversion of the adduct (**5c**) into the hydrazine (**7**) was attempted using activated zinc in a mixture of acetic acid and tetrahydrofuran, conditions which are known to cleave trichloroethylurethanes.[7] This was followed by *in situ* oxidation using copper(II) chloride. However, the only product isolated from the reaction was the *cis*-cinnamate (**9**), a known oxidation product of the 3a*H*-indene (**4a**),[3] and a possible pathway for its formation is shown in Scheme 2.

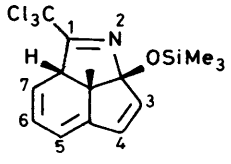


Scheme 2.

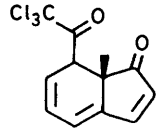
Evidence for the intermediacy of the 3a*H*-indene (**4a**), presumably formed by loss of nitrogen from the cyclic azo compound (**8**), was obtained by repeating the reaction in the presence of *N*-phenylmaleimide whereupon the adduct (**3**) was obtained in 26% yield.

Addition to C≡N *Bonds.*—Nitriles bearing electron withdrawing groups possess a relatively reactive C≡N bond, and we therefore investigated the cycloaddition of such nitriles to the 3a*H*-indenes (**4**).

Generation of the 3a*H*-indene (**4a**) from the adduct (**3**) at 110 °C in the presence of methyl cyanoformate gave only the *exo*- and *endo*-[8 + 2] *N*-phenylmaleimide adducts,[2] indicating that methyl cyanoformate is not sufficiently reactive to compete with the liberated *N*-phenylmaleimide. Repetition of the reaction using trichloroacetonitrile as the 2π-component resulted in a complex mixture. However, reaction of this nitrile with the 3-trimethylsiloxy-3a*H*-indene (**4b**) was slightly more successful in that the required [8 + 2]-adduct (**10**) was obtained, albeit in poor yield, together with 1-methyl-1-trimethylsiloxy-1*H*-indene, the rearrangement product of (**4b**),[2] from which it was inseparable. The regiochemistry of the cycloaddition, which is as expected on the basis of our earlier results, was suggested by the position of 7a-H of the adduct at δ 3.65 in its ^1H n.m.r. spectrum, and was confirmed by acid hydrolysis which gave the diketone (**11**). The diketone (**11**) was identified by its close similarity to the corresponding dichloromethyl compound, which we had previously prepared.[2]



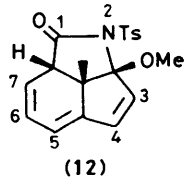
(10)



(11)

Addition to the C=N *Bond of Isocyanates.*—Isocyanates are known to participate in [$\pi^2s + \pi^2a$] cycloaddition reactions with alkenes and 1,3-dienes.[8,9] The formally allowed $\pi^2s + \pi^4s$ reaction does not occur with simple 1,3-dienes, and although [4 + 2]-adducts are often isolated, these are formed by rearrangement of the initial [2 + 2]-adducts.[9] Reaction of the 3a*H*-indene (**4a**) with toluene-*p*-sulphonyl isocyanate and the highly reactive chlorosulphonyl isocyanate[9] was therefore of particular interest because of the [2 + 2], [4 + 2], and [8 + 2] cycloaddition modes that are possible.

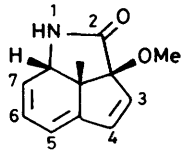
Thermal generation of the 3a*H*-indene (**4a**) from compound (**3**) in the presence of toluene-*p*-sulphonyl isocyanate gave a 43% yield of a 1:1 adduct which, on the basis of its spectral properties, was assigned the structure (**12**), the regiochemistry being as expected. The same reaction was attempted preparing the 3a*H*-indene (**4a**) from the trienone (**2**), but this gave only a trace of the adduct (**12**), presumably because of the much lower reaction temperature.



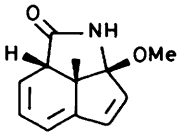
(12)

Chlorosulphonyl isocyanate (CSI) is one of the most reactive isocyanates known,[9] and reacts readily with alkenes and polyenes *via* either a concerted $\pi^2s + \pi^2a$ mechanism or *via* 1,4-dipolar intermediates, the exact mechanism depending on the substrate.[9–12] Of particular interest was the report that CSI reacted with 7-methylenecyclo-octa-1,3,5-triene to give an [8 + 2]-adduct, presumably *via* a 1,4-dipolar intermediate,[13] and therefore, on this basis and by analogy with the reaction with toluene-*p*-sulphonyl isocyanate, the 3a*H*-indene (**4a**) was expected to react with CSI to give an [8 + 2] adduct. In the event, 3-methoxy-3a-methyl-3a*H*-indene (**4a**), prepared from the trienone (**2**), reacted with CSI to give, after *in situ* hydrolysis

of the chlorosulphonyl group using aqueous sodium sulphite–sodium hydrogen carbonate, a mixture (57%) of the possible [8 + 2]-cycloadducts (**13**) and (**14**) in the ratio 2.5:1.* The ^{1}H n.m.r. spectrum of the major adduct in which 7a-H resonated at δ 4.12 [*cf.* 7a-H of compound (**12**) at δ 3.04] suggested that this adduct had the structure (**13**).



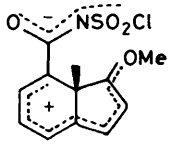
(13)



(14)

This result was surprising in that the regiochemistry of the addition of CSI to (**4a**) was expected to parallel that of toluene-*p*-sulphonyl isocyanate, to give largely the adduct (**14**). A nuclear Overhauser effect (n.O.e.) difference experiment confirmed the structural assignments, pre-irradiation of the NH signal (δ 7.25) of the major isomer causing an enhancement of the signal attributed to 7a-H at δ 4.12, and *vice versa*. Pre-irradiation of the other NH signal (δ 7.84) resulted in enhancement of the corresponding minor methoxy signal at δ 3.39, establishing the minor isomer as the structure (**14**).

The formation of the 'expected' isomer (**14**) proably occurs *via* the dipolar intermediate (**15**) which can collapse to give the observed product, after hydrolysis. It is possible that the major regioisomer (**13**) is formed by a concerted thermally allowed [8 + 2] cycloaddition.



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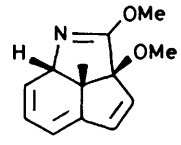

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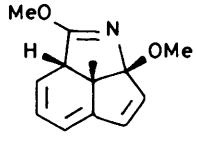
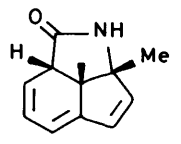


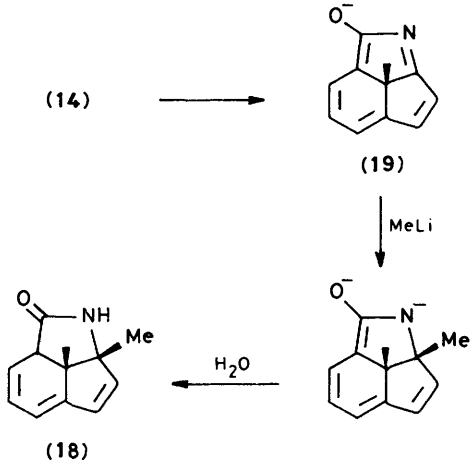
(17)



(18)

The cyclic amide (**13**) was readily converted into the corresponding imidiate (**16**) by treatment with methyl fluorosulphonate and triethylamine. Repetition of the reaction with the inseparable mixture of amides (**13**) and (**14**) gave the expected mixture of imidiates (**16**) and (**17**) which, unfortunately, were also inseparable.

In connection with our work on [10]annulenes[14] it was reasoned that elimination of the elements of methanol from the imidates (**16**) and (**17**) should give aza derivatives of the aromatic tricyclic [10]annulene system. However, these elimination reactions could not be effected under a variety of acidic (toluene-*p*-sulphonic acid) and basic (DBU, MeLi, or LDA) conditions. An attempt was also made to eliminate methanol from the amides (**13**) and (**14**). Thus the mixture of amides (**13**) and (**14**) was treated with an excess of methyl-lithium at room temperature in tetrahydrofuran. Subsequent work-up gave a 25% yield of a product derived from the minor isomer (**14**). The ^{1}H n.m.r. spectrum of the product showed 7a-H at δ 2.86, and that the methoxy group had been lost but an extra methyl group had been incorporated. The product was assigned the structure (**18**), the stereochemistry of the methyl group at 2a-C being confirmed by n.O.e. difference experiments. Pre-irradiation of the central methyl group at δ 0.92 caused enhancements in both 7a-H and the extra methyl group at δ 1.38. A possible mechanism for the formation of (**18**) from amide (**14**) is shown in Scheme 3, and involves deprotonation followed



Scheme 3.

by loss of methanol to generate the 10π-aromatic anion (**19**). In the all-carbon tricyclic [10]annulene[14] there is considerable ring strain associated with position-2a, and although this ring strain is offset by the annulene resonance energy, in the present case the imine bond at N(2)–C(2a) in (**19**) is sufficiently reactive to undergo nucleophilic attack by methyl-lithium to give, after work-up, the observed product (**18**).

These cycloaddition reactions thus give the complete ring skeleta of 1-aza, 2-aza, and 1,2-diaza analogues of the tricyclic [10]annulene 7b-methyl-7b*H*-cyclopent[*cd*]indene. However, various attempts at aromatisation, to form the aza-annulenes, were unsuccessful.

Experimental

For general points see ref. 2.

Cycloaddition of the 3a*H*-*Indene* (**4a**) *to Dimethyl Azodicarboxylate*.—A solution of dimethyl azodicarboxylate (1.20 g, 8.2 mmol) in dry DME (6 ml) was added to a stirred solution of the 3a*H*-indene (**4a**) in DME, prepared [3] from the trienone (**2**) (1.10 g, 7.5 mmol). The mixture was filtered through Celite, and stirred overnight at room temperature. Further azo ester (0.30 g, 2.05 mmol) was added and the mixture was stirred until t.l.c. indicated the complete disappearance of (**4a**). The solvent was evaporated, and the residue chromatographed to give *dimethyl* 2,2a,7a,7b-*tetrahydro*-2a-*methoxy*-7b-*methyl*-1H-*cyclopent*-[cd]*indazole*-1,2-*dicarboxylate* (**5a**) (1.13 g, 49%), m.p. 77—78 °C (Found: C, 58.8; H, 5.9; N, 9.1. $C_{15}H_{18}N_2O_5$ requires C, 58.8; H, 5.9; N, 9.15%); $\nu_{max.}$(CCl_4) 1 710 cm^{-1}; $\lambda_{max.}$(EtOH) 296 nm (log ε 3.81); δ_H (250 MHz; $CDCl_3$), 1.06 (3 H, s), 3.52 (3

* On the first attempt this reaction gave adduct (**13**) only, and this was isolated pure (see Experimental section). Thereafter, using a different and purer batch of CSI, an inseparable mixture of adducts (**13**) and (**14**) was produced.

H, s), 3.65 (3 H, s), 3.80 (3 H, s), 4.33 (1 H, d, *J* 6.0 Hz), 5.91 (1 H, d, *J* 5.6 Hz), 5.99 (1 H, m), 6.20 (1 H, dd, *J* 9.5, 5.6 Hz), 6.41 (1 H, d, *J* 5.6 Hz), and 6.62 (1 H, m); δ_C (62.9 MHz; $CDCl_3$) 17.7, 53.0 (2 overlapping lines), 53.4, 55.9, 60.7, 105.2, 114.4, 122.1, 126.2, 131.9, 132.9, 145.2, 154.9, and 158.0; *m/z* 306 (M^+).

Dimethyl 1-(7,7a-*Dihydro*-7a-*methyl*-1-*oxo*-1H-*inden*-7-*yl*)-*hydrazine*-1,2-*dicarboxylate* (**6a**).—The adduct (**5a**) (92 mg) was dissolved in a mixture of acetonitrile (5 ml), water (5 ml) and concentrated sulphuric acid (2 drops). The mixture was stirred for 18 h, poured into water and extracted with chloroform (3 × 30 ml). The combined extracts were dried and evaporated to give the *title compound* (**6a**) (85 mg, 97%), b.p. 100—105 °C at 0.2 mmHg (Kugelrohr) (Found: C, 57.2; H, 5.6; N, 9.3. $C_{14}H_{16}N_2O_5$ requires C, 57.5; H, 5.5; N, 9.6%); $\nu_{max.}$(CCl_4) 3 495, 1 767, 1 730, and 1 710 cm^{-1}; δ (250 MHz; $CDCl_3$) 1.23 (3 H, s), 2.35 (1 H, br), 3.64 (3 H, s), 3.73 (3 H, br s), 4.84 (1 H, br), 6.09 (1 H, br), 6.16 (1 H, d, *J* 5.2 Hz), 6.25 (1 H, d, *J* 5.7 Hz), 6.39 (1 H, dd, *J* 9.3, 5.3 Hz), and 7.74 (1 H, d, *J* 5.7 Hz); *m/z* 292 (M^+), 275, 217, and 145.

Cycloaddition of the 3aH-*Indene* (**4b**) *to Dimethyl Azodicarboxylate.*—Triethylamine (0.4 ml, 3 mmol) and trimethylsilyl trifluoromethanesulphonate (0.56 ml, 3 mmol) were added to a solution of the trienone (**2**) (0.40 g, 2.7 mmol) in dry ether (20 ml) at 0 °C, and the mixture was stirred under nitrogen for 1 h. Dimethyl azodicarboxylate (0.88 g, 6 mmol) was then added and the solution warmed to room temperature and stirred for 3 h. The mixture was poured into water and extracted with ether (3 × 40 ml). The combined extracts were evaporated, and the residue dissolved in a mixture of THF (18 ml) and water (6 ml) containing potassium fluoride (200 mg). The resulting solution was stirred for 3 h, diluted with water, and extracted with ether. The ether extracts were dried, evaporated and the residue chromatographed to give (i) *dimethyl* 2,2a,7a,7b-*tetrahydro*-7b-*methyl*-2a-*trimethylsiloxy*-1H-*cyclopent*[cd]-*indazole*-1,2-*dicarboxylate* (**5b**) (100 mg, 10%) as an oil, b.p. 95—98 °C at 0.15 mmHg (Kugelrohr) (Found: C, 55.7; H, 6.6; N, 7.5. $C_{17}H_{24}N_2O_5Si$ requires C, 56.0; H, 6.6; N, 7.7%); $\nu_{max.}$(CCl_4) 1 743 and 1 710 cm^{-1}; δ (250 MHz; $CDCl_3$) 0.18 (9 H, s), 0.97 (3 H, s), 3.58 (3 H, s), 3.72 (3 H, s), 4.28 (1 H, d, *J* 5.3 Hz), 5.86 (1 H, d, *J* 5.3 Hz), 5.98 (1 H, m), 6.15 (1 H, dd, *J* 9.4, 5.3 Hz), 6.31 (1 H, d, *J* 5.3 Hz), and 6.38 (1 H, br); *m/z* 364 (M^+); and (ii) the ketone (**6a**) (250 mg, 31%).

Cycloaddition of the 3aH-*Indene* (**4a**) *to Bistrichloroethyl Azodicarboxylate.*—A mixture of the adduct (**3**) (100 mg, 0.29 mmol) and bistrichloroethyl azodicarboxylate (223 mg, 0.59 mmol) in toluene was heated under reflux for 30 min. The solvent was evaporated and the residue chromatographed to give *bistrichloroethyl* 2,2a,7a,7b-*tetrahydro*-2a-*methoxy*-7b-*methyl*-1H-*cyclopent*[cd]*indazole*-1,2-*dicarboxylate* (**5c**) (100 mg, 63%) as a viscous oil (Found: M^+, 537.91915. $C_{17}H_{16}Cl_6N_2O_5$ requires *M*, 537.9190); $\nu_{max.}$(neat) 1 755 and 1 725 cm^{-1}; δ_H [250 MHz; $(CD_3)_2SO$; 90 °C] 1.04 (3 H, s), 3.52 (3 H, s), 4.42 (1 H, d, *J* 5.5 Hz), 4.67 (1 H, d, *J* 12.2 Hz), 4.85 (1 H, d, *J* 12.2 Hz), 4.87 (1 H, d, *J* 12.2 Hz), 4.97 (1 H, d, *J* 12.2 Hz), 5.98 (1 H, dd, *J* 9.3, 5.5 Hz), 6.01 (1 H, d, *J* 5.5 Hz), 6.27 (1 H, dd, *J* 9.3, 5.5 Hz), 6.58 (1 H, d, *J* 5.8 Hz), and 6.63 (1 H, d, *J* 5.8 Hz); δ_C (62.9 MHz; $CDCl_3$) 17.7, 53.4, 55.8, 60.4, 75.0, 75.5, 76.5, 95.1, 115.1, 121.4, 121.7, 126.4, 131.8, 132.2, 132.8, 144.4, and 152.5.

Cycloaddition of the 3aH-*Indene* (**4b**) *to Bistrichloroethyl Azodicarboxylate.*—Triethylamine (0.52 ml, 3.9 mmol) and trimethylsilyl trifluoromethanesulphonate (0.7 ml, 3.8 mmol) were added to a solution of the trienone (**2**) (0.50 g, 3.4 mmol) in dry ether (25 ml), and the mixture was stirred at 0 °C under nitrogen for 1 h. Bistrichloroethyl azodicarboxylate (2.87 g, 7.5 mmol) was added, and the mixture stirred at room temperature overnight. The mixture was poured into water, extracted with ether, and the ether extracts were dried and evaporated. The residue was chromatographed to give *bistrichloroethyl* 1-(7,7a-*dihydro*-7a-*methyl*-1-*oxo*-1H-*inden*-7-*yl*)*hydrazine*-1,2-*dicarboxylate* (**6b**) (745 mg, 41%) (Found: M^+, 523.9042. $C_{16}H_{14}Cl_6N_2O_5$ requires M^+, 523.9034); $\nu_{max.}$(CCl_4) 3 400, 1 785, 1 742, and 1 710 cm^{-1}; δ (90 MHz; $CDCl_3$) 1.28 (3 H, s), 4.4—5.1 (5 H, m), 6.0—6.6 (4 H, m), 6.74 (1 H, br), and 7.72 (1 H, d, *J* 5.3 Hz).

Attempted Cleavage of the Adduct (**5c**).—(*a*) The adduct (**5c**) (0.10 g, 0.19 mmol) was dissolved in glacial acetic acid (5 ml) and the reaction solution purged with nitrogen. After cooling to 0 °C, dry THF (5 ml) and activated zinc (0.75 g, 11.5 mmol) were added to the reaction mixture which was stirred for 2 h. It was then cooled to −30 to −40 °C for 0.5 h before being filtered under nitrogen. This gave a yellow filtrate which went orange with time. The volume of the filtrate was reduced and it was then added to the aqueous filtrate obtained from washing the zinc with water. The combined extracts were acidified to pH 3 using hydrochloric acid (1.0M). Copper(II) chloride (2M solution; 0.5 ml, 1 mmol) was added and the solution was stirred for 0.5 h. Ammonium hydroxide was then added until the pH of the solution was 5. This was then extracted with chloroform (3 × 30 ml) and the combined extracts were washed with sodium hydrogen carbonate, dried, and evaporated. The residue was subjected to column chromatography to give methyl 2-methyl-*cis*-cinnamate (**9**) (5 mg, 15%).

(*b*) *In the presence of* N-*phenylmaleimide.* The adduct (**5c**) (114 mg) was dissolved in acetic acid (5 ml) and the reaction flask purged with nitrogen. The solution was cooled to 0 °C and THF (5 ml) was added. Activated zinc (0.83 g, 12.7 mmol) was then transferred to the reaction vessel and the solution was observed to turn yellow. After being stirred at 0 °C for 2 h the solution was filtered under nitrogen. *N*-Phenylmaleimide (0.039 g, 0.22 mmol) was added to the filtrate and the reaction mixture stirred for 0.5 h at room temperature. The pH of the solution was adjusted to 2 and copper(II) chloride (2M; 0.5 ml, 1 mmol) was added and stirring continued for 0.5 h. The reaction mixture was neutralised using ammonium hydroxide and extracted with chloroform. The combined extracts were dried and evaporated and the residue subjected to column chromatography. This gave the [4 + 2] *N*-phenylmaleimide adduct (**3**) (18 mg, 26%).

Cycloaddition of the 3aH-*Indene* (**4b**) *to Trichloroacetonitrile.*—A solution of 3a-methyl-3-trimethylsiloxy-3a*H*-indene (**4b**) was formed by the addition of triethylamine (0.1 ml, 0.75 mmol) and trimethylsilyl trifluoromethanesulphonate (0.14 ml, 0.75 mmol) to a stirred solution of the trienone (**2**) (100 mg, 0.68 mmol) in dry ether (15 ml) under nitrogen at 0 °C. The reaction mixture was stirred at this temperature for 1 h, trichloroacetonitrile (0.1 ml, 1 mmol) was added, and the solution refluxed for 4 h. T.l.c. analysis of the reaction indicated the presence of the 3a*H*-indene (**4b**) necessitating the further addition of trichloroacetonitrile (0.1 ml, 1 mmol). After being stirred at room temperature overnight the reaction mixture was poured into water (50 ml) and extracted with ether (3 × 40 ml). The combined extracts were dried, evaporated and the residue subjected to column chromatography to give a 1:2.5 mixture (70 mg) of (i) 1-methyl-1-trimethylsiloxy-1*H*-indene[2] and (ii) 7a,7b-dihydro-7b-methyl-1-trichloromethyl-2a-trimethylsiloxy-2aH-cyclopent[*cd*]isoindole (**10**) (*ca.* 20%), $\nu_{max.}$(CCl_4) 1 620 cm^{-1}; δ (250 MHz; $CDCl_3$) 0.22 (9 H, s), 0.91 (3 H, s), 3.63 (1 H, dd, *J* 6.3, 1 Hz), 5.97 (1 H, d, *J* 4.7 Hz), 6.03 (1 H, dd, *J* 8.9, 6.3 Hz), 6.21 (1 H, ddd, *J* 4.7, 8.9, 1 Hz), 6.37 (1 H, d, *J* 5.2 Hz), and 6.54 (1 H, d, *J* 5.2 Hz); *m/z* 362 (M^+).

7,7a-*Dihydro*-7a-*methyl*-7-*trichloroacetyl*-1H-*inden*-1-*one* (**11**).— The mixture of the adduct (**10**) and 1-methyl-1-trimethylsiloxy-1*H*-indene obtained as above (15 mg) was dissolved in benzene and toluene-*p*-sulphonic acid (8 mg) was added. The mixture was refluxed under nitrogen for 4 h, poured into water, and extracted with chloroform (3 × 20 ml). The chloroform extracts were dried, evaporated, and the residue chromatographed to give the *title compound* (**11**) (4 mg, 45%), as an oil (Found: M^+, 289.9667. $C_{12}H_9Cl_3O_2$ requires M^+, 289.9668); $\nu_{max.}$(CCl_4) 1 748 and 1 715 cm^{-1}; δ (250 MHz; $CDCl_3$) 1.15 (3 H, s), 4.25 (1 H, d, *J* 6.7 Hz), 6.17 (1 H, d, *J* 5 Hz), 6.28 (1 H, dd, *J* 9.2, 6.7 Hz), 6.43 (1 H, ddd, *J* 9.2, 5.0, 1.2 Hz), 6.49 (1 H, d, *J* 5.4 Hz), and 7.83 (1 H, d, *J* 5.4 Hz).

Cycloaddition of the 3aH-*Indene* (**4a**) *to Toluene*-p-*sulphonyl Isocyanate*.—A solution of the [4 + 2]-*N*-phenylmaleimide adduct (**3**) (223 mg, 0.67 mmol) in toluene-*p*-sulphonyl isocyanate (7 ml) was heated at 100 °C for 0.5 h under an atmosphere of nitrogen. The reaction mixture was poured into water (50 ml) extracted with ether (3 × 50 ml), and the combined extracts were washed with aqueous potassium hydroxide (2.5%; 50 ml), dried, and evaporated. The residue was subjected to column chromatography to give 2,2a,7a,7b-*tetrahydro*-2a-*methoxy*-7b-*methyl*-2-*toluene*-p-*sulphonyl*-1H-*cyclopent*[cd]*isoindol*-1-*one* (**12**) (103 mg, 43%) as a solid, m.p. 192—194 °C (Found: C, 64.1; H, 5.3; N, 4.0. $C_{19}H_{19}NO_4S$ requires C, 63.85; H, 5.4; N, 3.9%); $\nu_{max.}$(Nujol) 1 727, 1 590, 1 187, and 1 170 cm^{-1}; δ (250 MHz; $CDCl_3$) 1.0 (3 H, s), 2.39 (3 H, s), 3.04 (1 H, dd, *J* 6.8, 0.8 Hz), 3.61 (3 H, s), 5.86 (1 H, dd, *J* 9.1, 6.8 Hz), 5.91 (1 H, d, *J* 5.2 Hz), 6.15 (1 H, ddd, *J* 9.1, 5.2, 0.8 Hz), 6.61 (1 H, d, *J* 5.7 Hz), 6.85 (1 H, d, *J* 5.7 Hz), 7.24 (2 H, d, *J* 8.3 Hz), and 7.81 (2 H, d, *J* 8.3 Hz); *m*/*z* 357 (M^+).

Cycloaddition of the 3aH-*Indene* (**4a**) *to Chlorosulphonyl Isocyanate*.—(*a*) To a solution of the 3a*H*-indene (**4a**), prepared from the trienone (**2**) (1.60 g, 11 mol) was added chlorosulphonyl isocyanate (1.2 ml, 12 mmol). The reaction mixture was stirred for 2 h under an atmosphere of nitrogen before being filtered through Celite to remove the excess of potassium hydride. The solution was then poured into a mixture of aqueous sodium sulphite (10%, 100 ml), aqueous sodium hydrogen carbonate (10%, 100 ml) and ether (100 ml). After being stirred vigorously for 2 h, the resulting solution was extracted with ether (3 × 75 ml) and chloroform (50 ml). The combined extracts were dried, evaporated and subjected to column chromatography to give 1,2a,7a,7b-*tetrahydro*-2a-*methoxy*-7b-*methyl*-2H-*cyclpent*[cd]*indol*-2-*one* (**13**) (1.0 g, 45%) (Found: C, 70.4; H, 6.6; N, 6.6. $C_{12}H_{13}NO_2$ requires C, 70.9; H, 6.45; N, 6.9%); $\nu_{max.}$($CHCl_3$) 3 430 and 1 700 cm^{-1}; δ (250 MHz; $CDCl_3$) 1.07 (3 H, s), 3.54 (3 H, s), 4.12 (1 H, d, *J* 5.7 Hz), 5.68 (1 H, dd, *J* 8.9, 5.7 Hz), 5.85 (1 H, d, *J* 5.2 Hz), 6.21 (1 H, dd, *J* 8.9, 5.2 Hz), 6.46 (2 H, s), and 6.99 (1 H, br, D_2O exchangeable); *m*/*z* 203 (M^+).

(*b*) When the reaction was repeated thereafter the product was always an inseparable mixture (57%) of the adduct (**13**) and 2,2a,7a,7b-*tetrahydro*-2a-*methoxy*-7b-*methyl*-1H-*cyclopent*-[cd]*indol*-1-*one* (**14**) in the ratio 2.5:1; for compound (**14**), δ (250 MHz; $CDCl_3$) 1.02 (3 H, s), 2.99 (1 H, d, *J* 6.8 Hz), 3.40 (3 H, s), 5.90 (1 H, d, *J* 5.7 Hz), 5.92 (1 H, dd, *J* 9.1, 6.8 Hz), 6.31 (1 H, d, *J* 5.7 Hz), 6.43 (1 H, d, *J* 5.7 Hz), and 7.84 (1 H, br, D_2O exchangeable), other signal (1 H) obscured.

7,7a-*Dihydro*-2,2a-*dimethoxy*-7b-*methyl*-2aH-*cyclopent*[cd]-*indole* (**16**).—Methyl fluorosulphonate (0.06 ml, 0.75 mmol) **[CAUTION: HIGHLY TOXIC]** was added to a solution of the adduct (**13**) (114 mg, 0.56 mmol) in dry DME (15 ml). The mixture was stirred at room temperature for 12 h. Triethylamine (1 ml) was added, the solvent evaporated, and the residue chromatographed on alumina to give the *title compound* (**16**) (85 mg, 70%) as an oil (Found: M^+, 217.1108. $C_{13}H_{15}NO_2$ requires *M*, 217.1103); $\nu_{max.}$($CHCl_3$) 623 cm^{-1}; δ (250 MHz; $CDCl_3$) 1.02 (3 H, s), 3.40 (3 H, s), 3.83 (3 H, s), 4.23 (1 H, d, *J* 5.9 Hz), 5.86 (1 H, d, *J* 5.0 Hz), 6.06 (1 H, dd, *J* 9.3, 5.9 Hz), 6.20 (1 H, d, *J* 5.9 Hz), 6.22 (1 H, dd, *J* 9.3, 5.0 Hz), and 6.43 (1 H, d, *J* 5.9 Hz).

Mixture of the Imidates (**16**) *and* (**17**).—The mixture of [8 + 2] cycloadducts (**13**) and (**14**) (159 mg, 0.78 mmol) was dissolved in dry DME (10 ml) and stirred at room temperature under an atmosphere of nitrogen. Methyl fluorosulphonate (0.08 ml, 0.99 mmol) was added and the reaction mixture stirred for 6 h before triethylamine (0.3 ml) was added. The solution was then poured into water (15 ml) and extracted with ether (3 × 15 ml). The combined extracts were dried, evaporated, and the residue subjected to column chromatography to give an inseparable mixture of the imidates (**16**) and (**17**) (113 mg, 66%) in a ratio of 2:1, δ ($CDCl_3$, 90 MHz) minor component, 1.93 (3 H, s), 3.22 (1 H, d, *J* 6.5 Hz), 3.45 (3 H, s), 3.68 (3 H, s), and 5.7—6.65 (m).

2,2a,7a,7b-*Tetrahydro*-2a,7b-*dimethyl*-2a-*methoxy*-1H-*cyclopent*[cd]*isoindol*-1-*one* (**18**).—The mixture of cycloadducts (**13**) and (**14**) (141 mg, 0.7 mmol) was dissolved in dry THF (10 ml) and cooled to −78 °C under nitrogen. Methyl-lithium (1.2M; 2.9 ml, 3.5 mmol) was added and the mixture stirred at −78 °C for 30 min, before being allowed to warm to room temperature. The mixture was poured into water (15 ml), and extracted with ether (3 × 25 ml). The combined extracts were dried, evaporated, and the residue chromatographed to give the *title compound* (**18**) (32 mg, 25%), m.p. 163—166 °C (Found: C, 76.7; H, 7.0; N, 7.45. $C_{12}H_{13}NO$ requires C, 77.0; H, 7.0; N, 7.5%); $\nu_{max.}$(CCl_4) 3 180, 3 060, 2 975, 1 690, 1 382, 1 152, and 863 cm^{-1}; $\lambda_{max.}$(EtOH) 305 nm (log ε 3.69); δ_H (250 MHz; $CDCl_3$) 0.92 (3 H, s), 1.38 (3 H, s), 2.85 (1 H, dd, *J* 6.7, 1.0 Hz), 5.92 (1 H, dd, *J* 9.2, 6.7 Hz), 5.96 (1 H, d, *J* 5.2 Hz), 6.06 (1 H, d, *J* 5.4 Hz), 6.21 (1 H, ddd, *J* 9.2, 5.2, 1.0 Hz), 6.40 (1 H, d, *J* 5.4 Hz), and 6.52 (1 H, br, D_2O exchangeable); δ_C (62.9 MHz; $CDCl_3$) 16.8, 19.9, 45.9, 46.2, 70.4, 116.6, 120.5, 126.0, 133.8, 141.1, 149.3, and 175.6, *m*/*z* 187 (M^+), 144, and 129.

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