

Enamine Chemistry. Part 37.¹ Reaction of Methyl Vinyl Ketone with $\Delta^{1,8a}$ -2-Octalone Dienamines. Synthesis of Octahydro-1*H*-benzo[*d*]naphthalene-2,10(3*H*,11*H*)-diones and 9-Acetylperhydro-2,4a-ethanonaphthalen-3-ones

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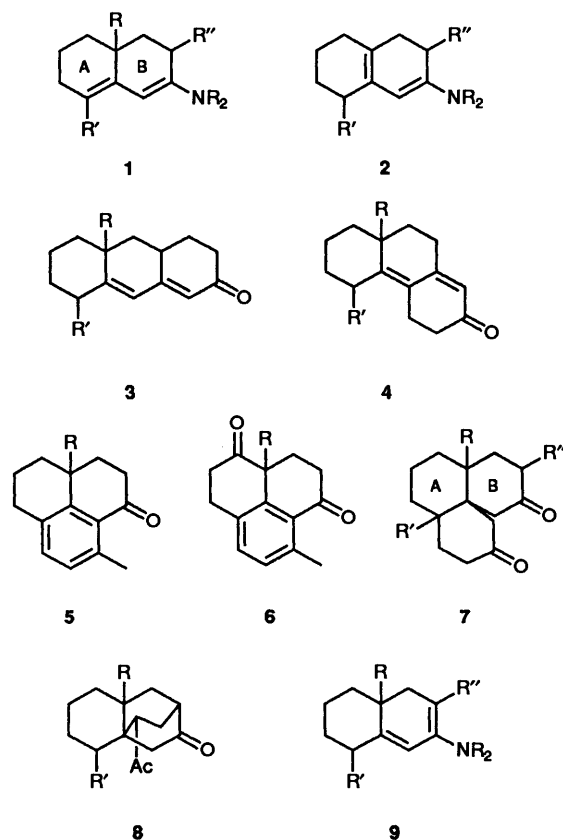
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Reaction of the pyrrolidine dienamines of $\Delta^{1,8a}$ -2-octalones with methyl vinyl ketone is complex. In methanol as solvent reaction occurs primarily with the linear dienamine isomer and results in annulation of the 8,8a-positions and, to a lesser extent, the 1,2-positions to give the corresponding octahydro-1*H*-benzo[*d*]naphthalene-2,10(3*H*,11*H*)-dione and 4,5,6,7,8,8a,9,10-octahydrophenanthren-2(3*H*)-one respectively. In toluene the dienamines react mainly in their cross-conjugated form. Diels–Alder addition of methyl vinyl ketone occurs across the 3,8a-positions to give the corresponding 9-acetylperhydro-2,4a-ethanonaphthalen-3-one, and annulation of the 2,3-positions gives the 4,4a,5,5a,6,7,8,9-octahydroanthracen-2(3*H*)-one. The mechanism of formation and spectral properties of the various products are discussed. Long-range shielding or deshielding effects arising from the proximity of stereochemically rigid C–C and C–H bonds are noted, the magnitude of which is sufficient to nullify or overcome the deshielding influence of neighbouring carbonyl groups.

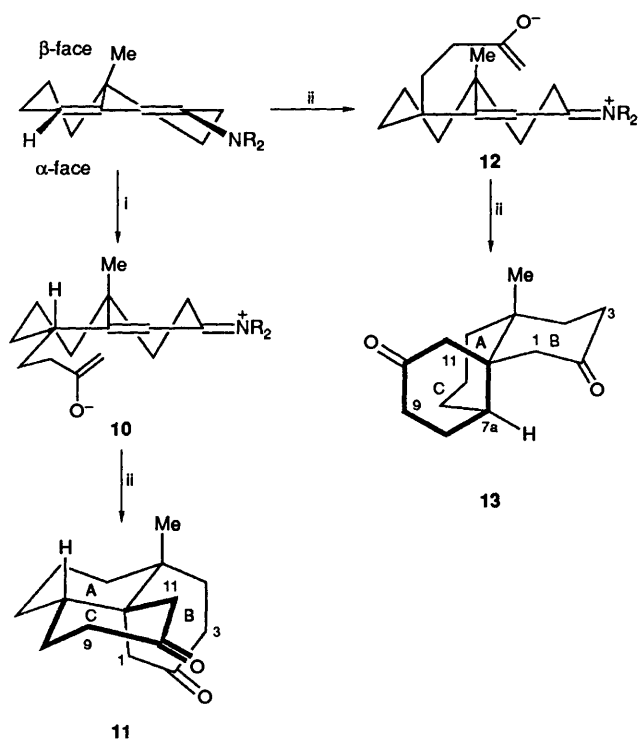
The Stork annulation² of substituted cyclohexanone enamines with methyl vinyl ketone to give the corresponding $\Delta^{1,8a}$ -2-octalones is well known and the regioselectivity of the reaction has been shown to be surprisingly sensitive to solvent effects in some cases.³ However, the further annulation of $\Delta^{1,8a}$ -2-octalones by the Stork reaction⁴ of their derived dienamines has not been investigated. Since we have shown previously⁵ that the dienamines of $\Delta^{1,8}$ -2-octalones exist as mixtures of the linear exocyclic (1) and linear endocyclic 2 double-bond isomers (R, R', R'' = H, Me) it was of interest to determine the course of their reaction with methyl vinyl ketone (MVK). We now report the results of this investigation.

In view of the polydentate nucleophilic properties of dienamines⁶ it was anticipated that their reaction with MVK would be complex and this has proved to be the case. The reactions were expected to give either the linear 3 or angular 4 annulation product (R, R' = H, Me), based on Stork's synthesis of $\Delta^{1,8}$ -2-octalones,² or compounds 5 by analogy with the reported synthesis of diones 6 from the corresponding 5-oxodienamine.⁷ In fact, structures of type 5 have not been isolated from any of the reactions we now report, and structures 3 and 4 have generally been the minor components of the complex reaction mixtures produced. The main products have proved to be the 8,8a-annulation product 7 (in methanol) or the [4 + 2] cycloaddition product 8 (in toluene). Interestingly, both products 3 and 8 are derived from the cross-conjugated dienamine 9 which we have previously⁵ failed to detect in the ¹H NMR spectra of the dienamine mixtures.

The first reaction we studied was that of the pyrrolidine dienamine of 4a-methyl- $\Delta^{1,8}$ -2-octalone since we expected that this would exist only as the linear dienamine 1 (R = Me, R' = R'' = H) and thereby simplify the course of the reaction. In boiling methanol as reaction solvent, the spectral data of the main product isolated showed the presence of two saturated carbonyl functions (δ_C 210.43 and 210.61) and one methyl group, and the absence of acetyl and tri- or tetra-substituted carbon–carbon double bonds. On the basis of this information and mechanistic reasoning, structure 7 (R = Me, R' = R'' = H) was proposed and subsequently confirmed by X-ray analysis of the crystal structure.⁸ The stereochemistry of the ring junctions is shown in structure 11 (Scheme 1). A second stereoisomer of this product was also isolated and later shown

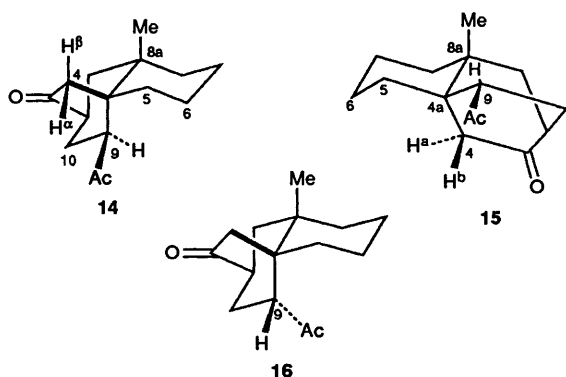


to be identical with the main product derived from the corresponding reaction with the dienamine of 8-methyl- $\Delta^{1,8a}$ -2-octalone (*vide infra*). The stereochemistry of this second isomer is indicated in structure 13 (Scheme 1). In each case the new ring which has been fused onto the existing bicyclic ring system is depicted in heavy lines. A third product, isolated in low yield (< 1%) from the complex reaction mixture, was identified from the spectral data as the angular annulation product, 8a-methyl-4,5,6,7,8,8a,9,10-octahydrophenanthren-2(3*H*)-one 4 (R = Me, R' = H). In toluene the reaction took an entirely different



Scheme 1 i, α -attack; ii, β -attack

course. The spectral data of the main product isolated again showed the presence of two saturated carbonyl functions (ν_{CO} 1710, 1730 cm^{-1} ; δ_{C} 212.60 and 216.56), two methyl groups (δ_{H} 0.94 and 2.3), and the absence of a carbon-carbon double bond. On this basis structure **8** ($\text{R} = \text{Me}$, $\text{R}' = \text{H}$) was assigned and subsequently confirmed by X-ray analysis.⁸ The stereochemistry of the ring junctions is shown in structure **14**. A second stereoisomer (**15** or **16**) of this product was isolated



but attempts to determine the stereochemistry by X-ray analysis were unsuccessful owing to twinning of the crystals. The stereochemistry of these two isomers, together with that of other Diels-Alder adducts isolated in the course of this work, is discussed later. A third product was also isolated, in low yield (4%), and assigned as the linear annulation product, 5a-methyl-4,4a,5,5a,6,7,8,9-octahydroanthracen-2(3H)-one **3** ($\text{R} = \text{Me}$, $\text{R}' = \text{H}$) on the basis of its spectral and analytical data (see Experimental section).

It therefore appears that the dienamine is reacting mainly as the linear double-bond isomer **1** ($\text{R} = \text{Me}$, $\text{R}' = \text{R}'' = \text{H}$) in methanol, but that reaction is occurring primarily at the less reactive δ -position (C-8) initially, to give product **7**, and only to a very small extent at the more reactive β -position (C-1) to give product **4**. This is especially remarkable in view of the fact

that we have previously shown that the corresponding reaction of methyl propenoate and propenenitrile with $\Delta^{1,8a}$ -2-octalone dienamines occurs only at the more reactive β -position (C-1) in protic solvents.⁹ A number of explanations could be offered for the greater δ -selectivity of MVK with respect to the aforementioned electrophilic alkenes, but without more evidence there seems little point in further speculation at this stage. The mechanism of the subsequent cyclisation is also not confirmed but most probably involves a prototropic shift in the initially formed enolate anion to give intermediate **10** or **12** (Scheme 1), and subsequent cyclisation onto C-8a of the eniminium salt to give product **11** or **13**, respectively, after hydrolysis. Alternatively, a *trans*-enamination process could be involved.¹⁰

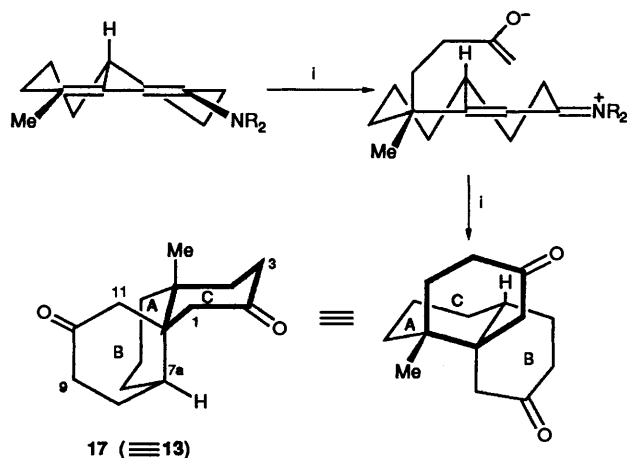
It is even more surprising that, in toluene, reaction occurs mainly with the cross-conjugated dienamine **9** ($\text{R} = \text{Me}$, $\text{R}' = \text{R}'' = \text{H}$) to give products **8** and **3**, especially since this dienamine must be present to such a small extent that we failed to detect its presence in earlier ¹H NMR studies of dienamines derived from $\Delta^{1,8a}$ -2-octalones.⁵ The only explanation we can offer is that in aprotic solvents, of low dielectric constant, charge separation in the ground and transition states is less favoured and the reaction becomes orbital controlled. In other words the activation energy for a [4 + 2] cycloaddition must be less than that for the formation of zwitterionic intermediates in an aprotic solvent, and the equilibrium **1** \rightleftharpoons **9** is displaced as isomer **9** undergoes cycloaddition. Ring opening of the Diels-Alder adduct, initiated by the 'push' of the enamine function and the 'pull' of the acetyl group, could subsequently lead to a zwitterionic intermediate after the dienamine equilibrium **1** \rightleftharpoons **9** has been displaced, and hence to the linear annulation product **3**.

The crystal structure⁸ of the main product **11** produced in methanol shows that initial attack by MVK occurred from the least hindered α -face, *anti* to the C-4a methyl group, as would be expected on steric grounds (Scheme 1). However, subsequent cyclisation at C-8a occurred from the β -face, *syn* to the 4a-methyl group. The developing steric interactions with the 4a-methyl group are alleviated by the B ring of the dienamine residue becoming *cis*-fused to the A ring, the new ring introduced by reaction with MVK being *trans* fused to the A ring by two equatorial bonds. This suggests that the transition state for formation of the second bond is late and that significant rehybridisation at C-8a has occurred in the transition state, otherwise cyclisation would presumably have to occur from the α -face to give a *cis*-fused new ring. Developing sp^3 -hybridised character at C-8a associated with a late or product-like transition state, as we have previously proposed in order to account for the relative stereoselectivity of protonation of enamines and enol ethers,¹¹ and a 'dropping away' of the 1-8a bond of the dienamine residue towards the α -face, would enable the terminal carbon of the MVK residue to approach the C-8a position at an angle to the axis of the C-4a-methyl bond and thus minimise developing steric interactions. In the formation of the minor isomer **13** (Scheme 1) initial attack at C-8 has occurred from the more hindered β -face, *syn* to the 4a-methyl group, but in this case cyclisation has also occurred from the β -face to give a *cis*-fused new ring attached by an axial and an equatorial bond to the A ring of the dienamine residue. However, instead of the 1-8a bond becoming axial to ring A it is now the 8-8a bond which has become axial to ring B of the dienamine residue in order to minimise steric interactions between the new ring and the 4a-methyl group.

The crystal structure,⁸ **14**, of the main product produced in toluene, **8** ($\text{R} = \text{Me}$, $\text{R}' = \text{H}$), shows that cycloaddition has also occurred from the α -face, *anti* to the 4a-methyl group as would be expected on steric grounds. However, since we were unable to obtain a crystal structure of the minor [4 + 2]

cycloaddition product it was not certain initially whether cycloaddition had occurred from the more hindered β -face, *syn* to the 4a-methyl group to give product **15**, or whether attack had again occurred from the less hindered α -face to give a diastereoisomer of compound **8** ($R = \text{Me}$, $R' = \text{H}$) (*i.e.*, structure **16**). This problem has now been resolved in favour of structure **15** (β -face attack). However, since there are some surprising features about the ^1H NMR spectra of the two isomers the reasons for this stereochemical assignment will be discussed later.

We next turned our attention to the reaction of MVK with the pyrrolidine dienamines of other $\Delta^{1,8a}$ -2-octalones, and in each case we found a similar trend. Reaction of MVK with the dienamine from 8-methyl- $\Delta^{1,8a}$ -2-octalone **1** ($R = R'' = \text{H}$, $R' = \text{Me}$) in methanol again gave a complex mixture, containing two isomeric forms of the tricyclic dione **7** ($R = R'' = \text{H}$, $R' = \text{Me}$). The main isomer was shown by X-ray analysis¹² to have structure **17** (25%; m.p. 158 °C) (Scheme 2) and is identical



Scheme 2 i, β -attack

in every respect with the minor isomer **13** isolated from the 4a-methyl- $\Delta^{1,8a}$ -2-octalone dienamine reaction. The minor component from the 8-methyl- $\Delta^{1,8a}$ -2-octalone dienamine reaction (2%) was not isolated but was shown by capillary GLC to be identical with the major component (m.p. 139–141 °C) from the 4a-methyl methanol reaction. The difference in the isomer ratios from the two reactions is undoubtedly due to there now being no steric impediment to β -face attack by the MVK at the C-8 position of the dienamine from 8-methyl- $\Delta^{1,8a}$ -2-octalone, since the new bond formed at C-8 is now *syn* to an axial hydrogen at C-4a, rather than to an axial methyl group at C-4a. Initial β -attack at C-8 is then followed by cyclisation from the β -face (Scheme 2) to give product **17** and construction of molecular models shows this product to be the same molecule as **13** (Scheme 1) the only difference being the new cyclohexanone ring (c) which has been fused on is the same as the existing cyclohexanone b ring in the product **13** derived from the 4a-methyl dienamine reaction, and *vice-versa*. Formation of the minor isomer from the 8-methyl dienamine reaction would involve α -face attack (not shown) on the dienamine and this would be less favourable on stereoelectronic grounds (*i.e.*, developing boat or twist-like conformations in the transition state). The angular annulation product **4** ($R = \text{H}$, $R' = \text{Me}$) was also isolated in low yield (7%) from this reaction.

In toluene, reaction again occurred mainly *via* the cross-conjugated dienamine isomer to give the Diels–Alder adduct **8** ($R = \text{H}$, $R' = \text{Me}$), isolated in two isomeric forms. Their stereochemistry is discussed later. The main difference between this reaction and the corresponding reaction with the 4a-methyl dienamine is that the linear annulation product **3** ($R = \text{H}$, $R' = \text{Me}$) was now the main product. This difference can

again readily be explained on steric grounds. In the formation of compound **3** ($R = \text{Me}$, $R' = \text{H}$) from the 4a-methyl dienamine, β -face (axial) attack at C-3 is hindered by the 4a-methyl group, and α -face (equatorial) attack is disfavoured on stereoelectronic grounds. In the formation of the regioisomer **3** ($R = \text{H}$, $R' = \text{Me}$) from the 8-methyl dienamine, β -face attack at C-3 is unimpeded with consequent increase in yield of the linear annulation product.

Reaction of MVK with the dienamine of 3-methyl- $\Delta^{1,8a}$ -2-octalone in methanol gave the tricyclic dione **7** ($R = R' = \text{H}$, $R'' = \text{Me}$). No angular annulation product was isolated and again this could be attributed to steric and stereoelectronic factors. The methyl group at C-3 would be axially orientated to minimise $A^{1,2}$ -strain,¹³ and thus impede reaction at C-1 but not C-8. The reaction in toluene was not studied.

Finally, the reaction of MVK with the pyrrolidine dienamine of $\Delta^{1,8a}$ -2-octalone was investigated. In methanol the tricyclic dione **7** ($R = R' = R'' = \text{H}$) was isolated in two isomeric forms [m.p. 133–135 °C (22%) and m.p. 165 °C (3%)]. There was also ~20% of a third component, which was not isolated pure but which is almost certainly the angular annulation product **4** ($R = R' = \text{H}$). In toluene equal proportions of Diels–Alder **8** ($R = R' = \text{H}$) and linear annulation **3** ($R = R' = \text{H}$) products were produced.

During the course of this latter work we became aware that House *et al.* had previously isolated the tricyclic diketone **7** ($R = R' = R'' = \text{H}$) as a by-product from the reaction of MVK with the pyrrolidine enamine of cyclohexanone.¹⁴ Our preliminary claim⁸ to have made the first synthesis of the tricyclo[8.4.0.0^{1,6}]tetradecane ring system is therefore incorrect.*

House *et al.* showed that their tricyclic ketone arose by 2,6-bis-alkylation of the pyrrolidine enamine of cyclohexanone by MVK in benzene, followed by a bis-cyclisation process. They specifically ruled out dienamines **1**, **2**, and **9** ($R = R' = R'' = \text{H}$) and $\Delta^{1,8a}$ -2-octalone as possible precursors to the tricyclic ketone. Despite the fact that their yield of tricyclic ketone rose considerably when they changed to ethanol as solvent, we rule out any possibility that our tricyclic diones could arise by a similar route since this would involve (i) hydrolysis of the dienamine under very mild conditions; (ii) ring opening; (iii) reformation of, in the case of the 4a- and 8-methyl dienamines, a 2,6- or a 2,2-disubstituted enamine; and (iv) further alkylation to give the enamine or iminium salt of a trisubstituted ketone (*i.e.*, 2-methyl-2,6-bis-(3-oxobutyl)cyclohexanone). Steps (iii) and (iv) for 2,2- or 2,6-disubstituted cyclohexanone enamines are rendered difficult, if not impossible, by developing $A^{1,3}$ -strain¹³ in a tertiary enamine, and would require forcing conditions.† Furthermore, the product isolated by House (m.p. 161–162 °C) corresponds to the minor isomer we isolated (m.p. 165 °C; 3% yield). If reversion of the dienamine to the monosubstituted cyclohexanone enamine had occurred in our reaction, followed by further alkylation and recyclisation, then this isomer should have been the major product. This is contrary to observation and confirms that tricyclic dione formation is occurring by δ -alkylation of the dienamines as indicated in Schemes 1 and 2.

One final observation of interest deserves comment. The NMR spectra of all the tricyclic products isolated were very complex. Even at 500 MHz several regions of the ^1H NMR spectrum consisted of overlapping areas of second-order splitting so a completely unequivocal proton assignment could

* We apologise to Professor House and his colleagues for previously overlooking their elegant synthetic work.

† We have previously prepared¹⁵ a secondary enamine (imine) of a 2,2-disubstituted cyclohexanone, with difficulty, *via* the TiCl_4 method.¹⁶

not be made. However, one or more of the protons alpha to the two carbonyl groups in structures **7** and **8** are sufficiently deshielded to appear outside the complex methylene envelope of the remaining protons and can be unequivocally assigned. In addition to stereochemical assignments, this has led to the observation of some surprising variations in chemical shifts arising from long-range shielding or deshielding effects associated with stereochemically rigid C–C and C–H single bonds.

In the 125 MHz ^{13}C NMR spectrum of the tricyclic ketone **13** (Scheme 1) the signals due to the C-1 and C-11 carbons can readily be assigned (δ_{C} 45.1, 46.15) since these are alpha to a carbonyl group and a quaternary centre and are therefore the lowest field methylene signals in the ^{13}C spectrum. The protons attached to these carbons (HETCOR) appear as doublets at δ 2.74, 2.42, 2.24, and 2.12 at 500 MHz. The two highfield doublets, at δ 2.24 and 2.12, are further split into weakly coupled doublets and triplets, respectively. This we attribute to W-coupling and allows unequivocal assignment of the signals to be made. The doublet of triplets at δ 2.12 is therefore assigned to the equatorial proton at C-11 which is W-coupled to the C-9 equatorial proton and the methine proton at C-7a (δ_{H} 1.83). This assignment has been confirmed by decoupling of the C-7a proton when the signal due to the C-11 equatorial proton collapses to a doublet of doublets. The axial proton at C-11, to which the equatorial proton is geminally coupled (COSY), appears as a sharp doublet at lower field (δ 2.74) than the equatorial proton despite the latter being in the plane, and under the deshielding influence, of the adjacent carbonyl group. Similarly at C-1, the equatorial proton is W-coupled to the equatorial proton at C-3 and is at higher field (δ_{H} 2.24) than the axial proton at C-1 which appears as a sharp doublet at δ_{H} 2.42.

The effect of alkyl substituents on the chemical shifts of cyclohexane ring protons has been summarised by Booth.¹⁷ The introduction of an equatorial methyl group causes considerable upfield shifts (0.3–0.5 ppm) in the signals of both axial and equatorial protons on the adjacent carbon, whereas an axial methyl group causes an upfield shift of an adjacent equatorial proton (\sim 0.4 ppm) and a downfield shift of the adjacent axial proton (\sim 0.2 ppm). A 1,3-diaxial interaction between an axial methyl group and an axial proton causes a downfield shift of the latter (0.2–0.3 ppm).¹⁸

If we assume that a ring residue has a similar effect to a methyl group then the lowfield shifts of the axial protons at C-1 and C-11 relative to the equatorial protons at these positions can be attributed primarily to a shielding of the equatorial protons by the adjacent equatorially and axially orientated ring residues. This would reduce or nullify the deshielding influence of the adjacent carbonyl group. Conversely the axial protons are deshielded by 1,3-diaxial-type interactions with ring residues (two for the C-11 axial proton) or 4a-methyl group (C-1 axial proton).

A similar, and perhaps even more surprising, effect of nearby ring residues on proton chemical shifts, is manifested in the [4 + 2] cycloadducts of MVK with the dienamine of 4a-methyl- $\Delta^{1,8a}$ -2-octalone (structures **14** and **15**). The structure of isomer **14** has been confirmed by X-ray analysis.⁸ The 200 MHz ^1H NMR spectrum shows a lowfield signal at δ 3.57 as an overlaid quartet of doublets and is assigned to 9-H. The splitting arises from vicinal coupling with the 10-H protons and W-coupling with the 4-H^b proton. At higher field there is a sharp doublet at δ 2.95 which shows no W-coupling and is therefore assigned 4-H^a since it is deshielded by being 1,3-diaxial to the acetyl group at C-9. This proton is geminal coupled (COSY) to a signal at δ 1.93 which appears as a doublet of doublets and is therefore assigned to 4-H^b. The structure of the stereoisomer **15** is assigned as shown since the 9-H signal again appears as a quartet of doublets (δ 3.04) due to vicinal and W-coupling.

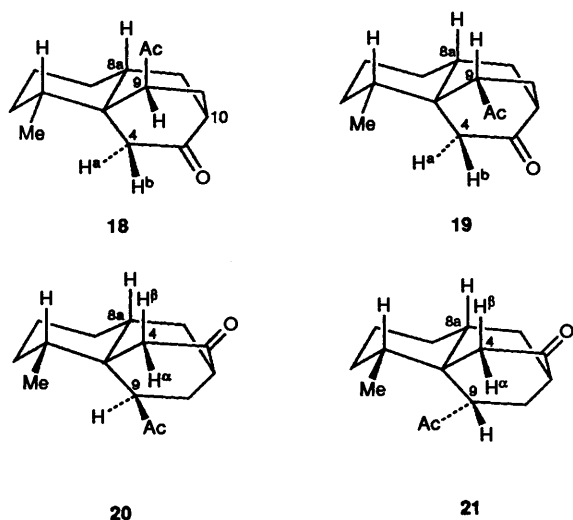
Structure **16**, a diastereoisomer of **14** which would have arisen from α -face attack of the dienamine at C-3 and C-8a, is unequivocally ruled out since the 9-H proton would not show W-coupling with any proton. The 200 MHz ^1H NMR spectrum of isomer **15** further shows a doublet of doublets at δ 2.59 and a sharp doublet at δ 2.14. The former signal is assigned to 4-H^a since it shows W-coupling (to 9-H) and the latter to 4-H^b. So again we have the situation where the proton (4-H^a) which is furthest away from the deshielding effect of a carbonyl group is at lower field than a proton (4-H^b) which is 1,3-diaxial to the acetyl group at C-9. We again attribute this deshielding of 4-H^a to the axially orientated ring residue at C-8a and that at C-5 which has a similar 1,3-diaxial-type orientation to 4-H^a). More specifically, of course, the deshielding of the 4-H^a proton can be primarily attributed to intramolecular van der Waals's shifts arising from the 6-H and 8-H axial protons, both of which exert van der Waals's compression forces on 4-H^a, similar to the mutual deshielding of axial protons at positions 2, 4, 6 and 8 in *cis*-decalin.^{17,18} The 4-H^b proton signal in structure **14** is at higher field (δ 1.93) than the 4-H^a proton signal in isomer **15** since the former is 1,3-diaxial only to the C-8a methyl group whereas the latter (δ 2.59) is 1,3-diaxial to the two ring residues mentioned above. Perhaps even more surprising than this is the large difference in chemical shifts (0.81 ppm) between the two protons 4-H^a (δ 2.95) and 4-H^b (δ 2.14) 1,3-diaxial to the acetyl group in isomers **14** and **15**. We attribute this difference to the magnetic anisotropy of the 5–6 carbon–carbon bonds in the two isomers. The 4-H^a proton lies in the deshielding 'cone' of the 5–6 bond in compound **14**, whereas the 4-H^b proton lies in the shielding region of the 5–6 bond in structure **15**. Even so, these are surprising differences.

In the case of structure **11** both the equatorial and axial protons at C-1 and C-11 have a path for W-coupling, the former with the equatorial proton at C-3 or C-9, and the latter with each other. It was therefore not possible to distinguish between the two sets of protons by the presence or absence of long-range coupling and an unequivocal assignment of the ^1H NMR signals has not been attempted.

There are four stereoisomers (**18–21**) possible for the [4 + 2] cycloadducts from the 8-methyl- $\Delta^{1,8a}$ -2-octalone dienamine, but only two isomers were isolated, as amber oils. Structures **18** and **19** would arise from β -face attack, and structures **20** and **21** from α -face attack on the dienamine. The main difference to be expected in the ^1H NMR spectra of these isomers is that in every case except **18** 9-H should show evidence of W-coupling either to one of the C-4 protons or to 8a-H. One of the isomers we isolated gave a triplet at δ 3.07 which is assigned to 9-H, vicinally coupled to the C-10 protons and showing no splitting due to W-coupling. This is therefore assigned structure **18**. The other isomer showed three lowfield signals [at δ 2.94 (dd), 2.8 (qd), and 2.65 (dd)] due to 4-H and 9-H. All three protons therefore show W-coupling. The only stereoisomer where this is possible is structure **19**. In structure **20** 4-H^a would not be W-coupled, and in structure **21** neither of the C-4 protons would be W-coupled. The magnitude of the geminal coupling constants (19 Hz) has enabled us to assign the signals at δ 2.94 and 2.65 to the C-4 protons, and the magnitude of the W-coupling constants (2 and 1.5 Hz) means the latter (δ 2.65) signal is due to 4-H^a (W-coupled to 9-H) and the former (δ 2.94) is due to 4-H^b (W-coupled to 8a-H).

So both isomers have arisen by β -face attack, isomer **18** being slightly favoured over **19** presumably due to steric interactions between the C-9 acetyl group and the C-5 methyl group (presumed to be equatorial) in the latter.

In the [4 + 2] cycloaddition of MVK to the unsubstituted $\Delta^{1,8a}$ -2-octalone, only one stereoisomer was isolated but the stereochemistry has not been assigned.



The reaction of MVK with other dienamines is currently being studied, as is their corresponding reaction with phenyl vinyl ketone (PVK).

Experimental

¹³C NMR and ¹H NMR spectra were obtained with a Varian Associates Gemini 200 spectrometer, operating at 50 and 200 MHz, respectively, in CDCl₃ solutions, unless stated otherwise. *J* Values are given in Hz. IR spectra were recorded with a Shimadzu IR408 spectrometer and were calibrated against the 1601 cm⁻¹ peak of polystyrene film. Gas-liquid chromatographic analyses were carried out with a Varian 3400 gas chromatograph using ultra-high purity nitrogen as carrier gas (gas flow 30 cm s⁻¹), a 30 m glass capillary column (Phase PS 25S; film thickness 0.53 μm), and a flame ionisation detector.

Microanalyses and GC-MS determinations were carried out by the Chemistry Department of the University of Natal, Pietermaritzburg, and accurate mass measurements by the Mass Spectrometry Unit, Cape Town. Silica gel (0.2 mm) containing fluorescent indicator (F₂₅₄) on aluminium-backed plates (Merck: Art. 5554) was used for TLC, and silica gel (Merck: Art. 9385) was used for flash chromatography.¹⁹

Δ^{1,8a}-2-Octalone, 4a-methyl-Δ^{1,8a}-2-octalone, 8-methyl-Δ^{1,8a}-2-octalone, and 3-methyl-Δ^{1,8a}-2-octalone, and their derived pyrrolidine dienamines, were prepared by the literature methods.² MVK was dried and distilled before use.

General Method.—MVK (1.61–5.26 g; 0.023–0.074 mol) was added dropwise to a stirred solution of the dienamine (1 mol equiv.) in dry methanol or toluene (100–150 cm³) under nitrogen and the mixture was heated under reflux for 4 or 43 h, respectively. Hydrolysis was carried out by the addition of a solution of sodium acetate (5 g) and glacial acetic acid (10 cm³) in water (10 cm³) and the mixture was heated under reflux for a further 4–5 h or overnight if this was more convenient. Volatiles were removed under reduced pressure and the residue was extracted with diethyl ether (3 × 50 cm³). The combined extracts were washed successively with 2 mol dm⁻³ hydrochloric acid (3 × 50 cm³), saturated aq. sodium hydrogencarbonate (50 cm³), and saturated aq. sodium chloride (3 × 50 cm³), and dried (MgSO₄). Filtration and evaporation of the extract gave a multicomponent mixture which was analysed by GLC and purified by flash chromatography, the fractions being monitored by TLC. Details of the separations are given under each specific reaction. In this way the following reactions were carried out.

Reaction of MVK with the Pyrrolidine Dienamine of (i) 4a-Methyl-Δ^{1,8a}-2-Octalone. (a) *In methanol.* A portion of the crude product (3.66 g), isolated as a viscous brown oil, from the dienamine (5 g, 0.023 mol) was purified by flash chromatography with hexane–methylene dichloride–ethyl acetate (12:3:1) as the eluent. Forty-two fractions (~50 cm³ each) were collected, the eluent proportions changed to 6:3:1 and a further 31 fractions were collected. Fractions 55–65 were combined and evaporated to give (4aR*,7aS*,11aR*)-4a-methyl-octahydro-1H-benzo[d]naphthalene-2,10(3H,11H)-dione **11**† as a crystalline product (0.67 g, 12%), m.p. 139–141 °C (from hexane–ethyl acetate); *v*_{max}(CHCl₃)/cm⁻¹ 1715 (CO); δ_H(200 MHz) 1.1 (3 H, s, Me) and 1.15–2.75 (19 H, complex); δ_C(50 MHz) 21.16 (t), 22.41 (q, Me), 28.02 (t), 28.10 (t), 32.06 (t), 35.78 (s, C-4a), 35.92 (t), 37.27 (t), 38.04 (d, C-7a), 40.84 (t), 40.87 (t), 46.80 (t), 47.17 (s, C-11a), and 210.43 and 210.61 (s, C-2, -10) (Found: C, 76.8; H, 9.6%; M⁺, 234. C₁₅H₂₂O₂ requires C, 76.9; H, 9.5%; M, 234); GLC (180 °C) *t*_R 48.2 min. The crystal structure has been reported previously.⁸ Fractions 47–52 were combined and evaporated to give *stereoisomer* **13** of 4a-methyl-octahydro-1H-benzo[d]naphthalene-2,10(3H,11H)-dione as a crystalline product (0.48 g, 9%), m.p. 157–159 °C (from hexane–ethyl acetate); *v*_{max}(CHCl₃)/cm⁻¹ 1705; δ_H(500 MHz) 1.10 (3 H, s, Me), 1.37 (1 H, m), 1.43 (1 H, m), 1.53–1.78 (5 H, complex), 1.79–1.89 (2 H, m), 2.1–2.32 (5 H, complex), 2.36 (1 H, sextet), 2.42 (1 H, d, *J* 14), 2.5 (2 H, m), and 2.74 (1 H, d, *J* 14, axial 11-H); δ_C(125 MHz) 20.44 (t), 22.71 (q, Me), 27.10 (t), 27.24 (t), 33.00 (d, C-7a), 33.99 (t), 34.78 (t), 35.72 (s, C-4a), 36.12 (t), 37.97 (t), 45.10 (t), 46.15 (t), 48.77 (s, C-11a), 210.17 and 211.52 (s, C-2, -10) (Found: C, 76.5; H, 9.55%; M⁺, 234. C₁₅H₂₂O₂ requires C, 76.9; H, 9.5%; M, 234); GLC (180 °C) *t*_R 37.7 min. A partial assignment of the ¹H and ¹³C NMR spectra is discussed in the text. This compound was identical with that obtained from the corresponding reaction of the pyrrolidine dienamine of 8-methyl-Δ^{1,8a}-2-octalone and the stereochemistry is discussed in the text.

A third product was isolated as an oil from fractions 27–30 in low yield (<1%; GLC) and is tentatively assigned as the non-linear annulation product 8a-methyl-4,5,6,7,8,8a,9,10-octahydrophenanthren-2(3H)-one **4** (R = Me, R' = H); δ_H (60 MHz) 0.73–2.93 (complex methylene envelope), 1.23 (3 H, s, Me) and 6.16 (1 H, br s, =CH).

(b) *In toluene.* The crude product was isolated as a viscous brown oil (3.94 g). A portion was purified by flash chromatography as in (a). Twenty-eight (~50 cm³) fractions were collected initially (eluent proportions 12:3:1) and then a further 18 fractions (eluent proportions 6:3:1).

Fractions 24–31 were combined, evaporated, and washed with a little hexane to give 9-acetyl-8a-methylperhydro-2,4a-ethanonaphthalen-3-one **14** as a crystalline product (1.45 g, 28%), m.p. 95–97 °C (from hexane–ethanol); *v*_{max}(CCl₄)/cm⁻¹ 1710 and 1730; δ_H(200 MHz) 0.94 (3 H, s, Me), 1.30–1.85 (11 H, complex methylene envelope), 1.93 (1 H, dd, *J* 19 and 2, 4-H^β), 2.08 (1 H, overlaid, qd, 10-H), 2.3 (3 H, s, Ac), 2.35 (1 H, m, 2-H), 2.95 (1 H, d, *J* 19, 4-H^α), and 3.57 (1 H, overlaid qd, 9-H); δ_C(50 MHz) 21.38 (t), 21.56 (t), 22.94 (q, Me), 28.54 (t), 29.03 (t), 33.06 (q, COMe), 34.39 (s, C-4a or -8a), 36.79 (t), 41.34 (s, C-8a or -4a), 43.27 (t), 43.51 (d and t), 43.69 (d, C-9), and 212.60 and 216.56 (s, C-3 and MeCO) (Found: C, 76.7; H, 9.7%; M⁺, 234. C₁₅H₂₂O₂ requires C, 76.9; H, 9.5%; M, 234); GLC (180 °C) *t*_R 23.2 min. The crystal structure has been reported previously.⁸

Fractions 38–46 were combined, evaporated and washed with a little hexane to give the *stereoisomer* **15** of 9-acetyl-8a-

† Each product is a racemic mixture; R*/S* refer to the relative configurations of the chiral centres in one enantiomer.

methylperhydro-2,4a-ethanonaphthalen-3-one as a crystalline product (0.68 g, 13%), m.p. 80–82 °C (from hexane–ethanol); $\nu_{\max}(\text{CCl}_4)/\text{cm}^{-1}$ 1715 and 1730 (CO); $\delta_{\text{H}}(200 \text{ MHz})$ 1.21 (3 H, s, Me), 1.23–2.0 (12 H, methylene envelope), 2.12 (3 H, s, CO Me), 2.14 (1 H, d, J 19.5, 4-H^b), 2.24 (1 H, q, 2-H), 2.59 (1 H, dd, J 19.5 and 2, 4-H^a), and 3.04 (1 H, qd, J 9, 5, and 2, 9-H); $\delta_{\text{C}}(50 \text{ MHz})$ 21.18 (t), 21.47 (t), 24.98 (q, Me), 26.62 (t), 30.76 (t), 33.08 (s), 33.51 (q, MeCO), 38.04 (t), 39.62 (t), 40.57 (t), 41.70 (s), 43.30 (d, C-2), 49.07 (d, C-9), and 212.58 and 215.35 (s, C-3 and MeCO) (Found: C, 76.9; H, 9.6%; M^+ , 234.1615. $\text{C}_{15}\text{H}_{22}\text{O}_2$ requires C, 76.9; H, 9.5%; M , 234.1619); GLC (180 °C) t_{R} 27.5 min.

Attempts to obtain an X-ray analysis were unsuccessful owing to twinning of the crystals. The structure is discussed in the text.

Evaporation of fraction 22 gave a low yield of the linear annulation product 5a-methyl-4,4a,5,5a,6,7,8,9-octahydroanthracen-2(3H)-one **3** (R = Me, R' = H) (0.2 g, 4%); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1585, 1615 (C=C) and 1650 (CO); $\delta_{\text{H}}(200 \text{ MHz})$ 1.20 (3 H, s, Me), 1.1–2.75 (complex methylene envelope), 5.72 (1 H, d, J 2.5, =CH), and 5.90 (1 H, d, J 1.8, =CH); $\delta_{\text{C}}(50 \text{ MHz})$ 21.95 (t), 23.24 (q, Me), 27.79 (t), 30.19 (t), 31.87 (d, C-4a), 32.77 (t), 36.76 (s, C-5a), 38.08 (t), 42.06 (t), 45.96 (t), 122.52 and 122.81 (d, C-1 and -10), 159.40 and 160.15 (s, C-9a and -10a), and 201.06 (s, C-2) (Found: M^+ , 216.1514. $\text{C}_{15}\text{H}_{20}\text{O}$ requires M , 216.1514); GLC (180 °C) t_{R} 30.7 min.

(ii) 8-Methyl- $\Delta^{1,8a}$ -2-octalone.—(a) *In methanol*. A portion of the crude product (6.13 g) obtained from the dienamine (8.04 g, 0.036 mol) was purified by flash chromatography with hexane–methylene dichloride–ethyl acetate (2:1:0.5) as eluent. Fractions 30–40 were evaporated, combined, and treated with charcoal. The product, still impure, was subjected to further flash chromatography with the above solvents (in 5:3:2 proportions) as eluent. Twenty fractions were collected. Fractions 10–14 were combined and recrystallised to give (4aR*,7aR*,11aR*)-4a-methyloctahydro-1H-benzo[d]naphthalene-2,10(3H,11H)-dione † **17** as a crystalline product (2.10 g, 25%), m.p. 158 °C (from hexane–ethyl acetate); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1705 (CO); $\delta_{\text{H}}(200 \text{ MHz})$ 1.11 (3 H, s, Me), 1.3–1.9 and 2.1–2.6 (18 H, complex methylene envelope), and 2.75 (1 H, d, J 14, axial 11-H); $\delta_{\text{C}}(50 \text{ MHz})$ 20.48 (t), 22.77 (q, Me), 27.15 (t), 27.28 (t), 33.03 (d, C-7a), 34.04 (t), 34.83 (t), 35.76 (s, C-4a), 36.18 (t), 38.02 (t), 45.14 (t), 46.19 (t), 48.82 (s, C-11a), 210.25 and 211.62 (s, C-2 and -10) (Found: C, 76.6; H, 9.35%; M^+ , 234.1615. $\text{C}_{15}\text{H}_{22}\text{O}_2$ requires C, 76.9; H, 9.5%; M , 234.1619). This compound was identical with the stereoisomer of (4aR*,7aS*,11aR*)-4a-methyloctahydro-1H-benzo[d]naphthalene-2,10(3H,11H)-dione derived from the 4a-methyl- $\Delta^{1,8a}$ -2-octalone [reaction (i) (a)]. When the ^1H and ^{13}C NMR spectra of the latter were rerun at 200 MHz and 50 MHz, respectively, they were found to be superposable on the above ^1H and ^{13}C NMR spectra. There was no depression of m.p. on admixture, and GLC (230 °C) of the mixture gave a single sharp peak, t_{R} 9.66 min. GLC (180 °C) of the crude mixture prior to flash chromatographic purification showed the presence of a small amount (<2%) of the other isomer **11** obtained from the 4a-methyl- $\Delta^{1,8a}$ -2-octalone reaction.

A third product detected in the GLC analysis of the crude product has been tentatively identified as the non-linear annulation product, namely 5-methyl-4,5,6,7,8,8a,9,10-octahydrophenanthren-2(3H)-one **4** (R = H, R' = Me) (~7%); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1605 (C=C) and 1650 (CO); $\delta_{\text{H}}(80 \text{ MHz})$ 1.09 (d, Me), 1.0–3.45 (complex methylene envelope), and 5.65 (s, =CH); δ_{C} 19.01 (q, Me), 20.36 (t), 25.05 (t), 29.66 (t), 30.52

(t), 31.44 (d), 32.97 (t), 34.85 (d), 35.25 (t), 37.15 (t), 121.92 (d, =CH), 124.28 (s), 151.79 (s), 158.56 (s), and 200.14 (s, CO) (Found: M^+ , 216.1520. $\text{C}_{15}\text{H}_{20}\text{O}$ requires M , 216.1514); GLC (180 °C) t_{R} 31 min.

(b) *In toluene*. A portion of the crude product (5.26 g) obtained from the dienamine (5.0 g, 0.023 mol) was purified by flash chromatography with hexane–methylene dichloride–ethyl acetate (12:3:1) as eluent and 72 (~50 cm³ each) fractions were collected. Fractions 19–28 appeared as one spot on TLC but GLC indicated four components. GC/MS showed all components to have the same molecular ion (M^+ , 216). It was found possible to isolate only one component pure enough for analysis by evaporation of fractions 19–28, washing with a small amount of ethyl acetate in hexane, followed by recrystallisation several times from hexane. This gave the main component of the crude product mixture and this was identified as the linear annulation product 9-methyl-4,4a,5,5a,6,7,8,9-octahydroanthracen-2(3H)-one **3** (R = H, R' = Me) (0.86 g, 17%); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1585, and 1610 (C=C) and 1650 (CO); $\delta_{\text{H}}(200 \text{ MHz})$ 1.14 (3 H, d, J 8, Me), 1.01–2.48 (complex methylene envelope), 5.79 (1 H, s, =CH), and 6.02 (1 H, s, =CH); $\delta_{\text{C}}(50 \text{ MHz})$ 18.28 (q, Me), 25.49 (t), 29.93 (t), 34.56 (d), 35.66 (t), 36.06 (t), 37.52 (d), 37.61 (t), 37.86 (t), 38.50 (d), 120.46 (d), 123.15 (d), 159.55 (s), 160.59 (s), and 201.05 (s, C-2) (Found: M^+ , 216.1525. $\text{C}_{15}\text{H}_{20}\text{O}$ requires M , 216.1514). GLC (180 °C) showed one peak, t_{R} 31.40 min.

Fraction 39 gave an amber oil, which was identified as 9-acetyl-5-methylperhydro-2,4a-ethanonaphthalen-3-one **18** (0.48 g, 9%); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1710 (CO); $\delta_{\text{H}}(200 \text{ MHz})$ 0.94 (3 H, d, J 8, Me), 1.05–2.8 (complex methylene envelope), 2.25 (3 H, s, Ac), and 3.07 (1 H, t, J 8.8, 9-H); $\delta_{\text{C}}(50 \text{ MHz})$ 16.52 (q, Me), 25.49 (t), 27.96 (t), 31.06 (d), 31.22 (t), 31.64 (t), 31.95 (t), 33.18 (q, MeCO), 35.49 (d), 38.80 (t), 42.82 (d), 43.43 (s, C-4a), 49.97 (d), and 212.67 and 217.12 (s, C-3 and MeCO) (Found: M^+ , 234.1631. $\text{C}_{15}\text{H}_{22}\text{O}_2$ requires M , 234.1620); GLC (180 °C) t_{R} 20.1 min.

Fraction 48 also gave an amber oil, which was identified as diastereoisomer **19** of 9-acetyl-5-methylperhydro-2,4a-ethanonaphthalen-3-one (0.32 g, 6%); $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$ 1710 (CO); $\delta_{\text{H}}(200 \text{ MHz})$ 0.89 (3 H, d, J 8, Me), 0.93–2.4 (complex methylene envelope), 2.18 (3 H, s, Ac), 2.65 (1 H, dd, J 19 and 2, 4-H^a), 2.8 (1 H, overlaid qd, J 11, 7, and 2, 9-H), and 2.94 (1 H, dd, J 19 and 1.5, 4-H^b); $\delta_{\text{C}}(50 \text{ MHz})$ 14.98 (q, Me), 20.13 (t), 28.14 (t), 28.49 (t), 30.62 (q, MeCO), 30.88 (t), 31.48 (d), 31.82 (t), 32.48 (d), 40.60 (t), 40.98 (s), 42.78 (d), 49.66 (d), and 210.34 and 216.84 (s, C-3 and MeCO) (Found: M^+ , 234.1636. $\text{C}_{15}\text{H}_{22}\text{O}_2$ requires M , 234.1620); GLC (180 °C), t_{R} 25.3 min. The stereochemistry is discussed in the text.

(iii) 3-Methyl- $\Delta^{1,8a}$ -2-octalone.—(a) *In methanol*. The crude product was obtained as a viscous brown oil (4.81 g) from the dienamine (6.0 g, 0.027 mol). A portion of the crude oil was purified by flash chromatography with hexane–methylene dichloride–ethyl acetate (6:3:1) as eluent (35 \times ~50 cm³ fractions). The eluent proportions were changed to 6:3:2 and a further eight fractions were collected. TLC [hexane–methylene dichloride–ethyl acetate (6:3:1)] of fractions 17–20 showed one component but GLC showed the presence of four isomers (1.38 g, 22%) (t_{R} 29.2, 31.0, 31.9 and 37.6 min). Fractions 15–22 were combined and rechromatographed (eluent proportions 8:4:1; 31 \times 50 cm³ fractions). Fractions 13–20 developed crystals on storage surrounded by oil. GC/MS showed four components, all having a molecular ion at m/z 234. Repeated recrystallisation from hexane–ethanol removed two components (t_{R} 29.2 and 37.6 min). Spectroscopic analysis of the remaining two-component mixture showed: $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1705 (CO); $\delta_{\text{H}}(200 \text{ MHz})$ 1.00 and 1.01 (3 H, 2 \times d, J 6.45, Me groups of two isomers), 1.48–2.6 (18 H, complex methylene

† One enantiomer.

envelope), 1.93 (1 H, d, J 13), and 3.05 (1 H, dd, J 1.0 and 13); δ_C (50 MHz) 14.30 (q, Me), 20.28 (t), 26.22 (t), 27.62 (t), 28.04 (t), 32.64 (d), 36.63 (t), 39.55 (d), 40.24 (d), 40.83 (t), 47.74 (s), 49.57 (t), 50.3 (t), and 210.98 and 212.98 (s, CO) (Found: C, 76.9; H, 9.5%; M^+ , 234. $C_{15}H_{22}O_2$ requires C, 77.4; H, 9.7%; M , 234). This product is therefore assigned as a mixture of two stereoisomers of 3-methyloctahydro-1*H*-benzo[*d*]naphthalene-2,10(3*H*,11*H*)-dione **7** ($R = R' = H$, $R'' = Me$) (1.05 g, 17%). The corresponding reaction in toluene was not investigated.

(iv) $\Delta^{1,8a}$ -2-Octalone.—(a) *In methanol*. The crude product was obtained as a viscous brown oil (9.13 g) from the dienamine (15.0 g, 0.074 mol). GLC and TLC analysis showed a complex mixture of several components. A portion of the crude product was purified by flash chromatography with hexane–methylene dichloride–ethyl acetate (5:7:2) as eluent ($44 \times \sim 50$ cm³ fractions). Fractions 21–23 were combined on the basis of TLC, evaporated, redissolved in ethanol, and treated twice with charcoal, to give a new stereoisomer of octahydro-1*H*-benzo[*d*]naphthalene-2,10(3*H*,11*H*)-dione **7** ($R = R' = R'' = H$) (3.58 g, 22%), m.p. 133–135 °C (from hexane–ethyl acetate); ν_{max} (CCl_4)/cm⁻¹ 1720 (CO); δ_H (200 MHz) 1.6–2.15 (14 H, complex methylene envelope), 2.0 (2 H, d, J 14, 1- and 11- H^{ax}), 2.35 (4 H, t, J 7, 3- and 9- H_2), and 2.75 (2 H, d, J 14, 1- and 11- H^{eq}); δ_C (50 MHz) 20.27 (2 t), 26.52 (2 t), 27.52 (2 t), 35.84 (d, C-7a and -4a), 38.85 (2 t), 46.95 (s, C-11a), 50.02 (2 t), and 210.77 (s, C-2 and -10) (Found: C, 76.1; H, 9.3%; M^+ , 220.1463. $C_{14}H_{20}O_2$ requires C, 76.3; H, 9.15%; M , 220.1463); GLC (180 °C) showed one peak, t_R 28.7 min.

A second product was isolated from fractions 37–41 and was assigned as a stereoisomer of octahydro-1*H*-benzo[*d*]naphthalene-2,10(3*H*,11*H*)-dione (0.46 g, 3%), m.p. 164.9–165 °C (from hexane–ethyl acetate) (lit.,¹⁴ 161–162 °C); ν_{max} ($CHCl_3$)/cm⁻¹ 1710 (CO); δ_H (200 MHz) 1.24–2.53 (complex methylene envelope); δ_C (50 MHz) 26.01 (t), 26.62 (t), 26.82 (t), 27.86 (t), 28.16 (t), 36.97 (t), 40.38 (t), 41.38 (t), 41.84 and 44.21 (d, C-4a and -7a), 45.14 (s, C-11a), 52.05 (t), and 209.81 and 210.74 (s, C-2 and -10) (Found: M^+ , 220.1453. Calc. for $C_{14}H_{20}O_2$: M , 220.1463); GLC (180 °C) showed one peak, t_R 34.1 min.

GLC of the crude product showed a third component (t_R 26.3 min) present to the extent of 20%. Attempts to isolate this component in a pure state by flash chromatography were unsuccessful.

(b) *In toluene*. The crude product was isolated as an amber oil (6.58 g) from the dienamine (7.0 g, 0.034 mol). A portion was purified by flash chromatography with the same eluent (proportions 12:3:1) ($82 \times \sim 50$ cm³ fractions). Fractions 35–56 were evaporated and washed with small amount of hexane to give 9-acetylperhydro-2,4a-ethanonaphthalen-3-one **8** ($R = R' = H$) (2.02 g, 27%) as a crystalline solid, m.p. 79–81 °C (from hexane–ethanol); ν_{max} (CCl_4)/cm⁻¹ 1705 and 1720 (CO); δ_H (200 MHz) 1.17–2.20 (complex methylene envelope), 2.21 (3 H, s, Ac), 2.28 (1 H, m), 2.41 (2 H, m), and 2.80 (1 H, t); δ_C (50 MHz) 21.27 (t), 25.41 (t), 27.31 (t), 30.35 (t), 31.16 (t), 33.05 (q, Me), 34.16 (t), 37.48 (t), 38.34 (d, C-8a), 39.09 (s, C-4a), 42.22 and 54.29 (d, C-2 and -9), and 212.23 and 215.48 (s, C-3 and MeCO) (Found: C, 76.6; H, 9.3%; M^+ , 220. $C_{14}H_{20}O_2$ requires C, 76.3; H, 9.15%; M , 220); GLC (180 °C) showed one peak, t_R 20.0 min. Fractions 10–27 were combined and rechromatographed (eluent proportions 24:4:1) ($35 \times \sim 50$ cm³ fractions). The eluent was then changed (proportions 12:3:1)

(25 × 50 cm³ fractions). Fractions 31–50 were combined and rechromatographed again (proportions 12:3:1) (43×50 cm³ fractions). Fractions 22–30 were combined, evaporated and washed with a small amount of hexane to give 4,4a,5,5a,6,7,8,9-octahydroanthracen-2(3*H*)-one **3** ($R = R' = H$) (1.92 g, 28%), m.p. 103 °C (from hexane–ethanol) (lit.,²⁰ 103 °C); ν_{max} (CCl_4)/cm⁻¹ 1590, 1625 (C=C), and 1670 (CO); δ_H (200 MHz) 0.95–2.53 (complex methylene envelope), 5.73 (1 H, s, =CH), and 5.98 (1 H, s, =CH); δ_C (50 MHz) 25.61 (t), 27.02 (t), 30.0 (t), 34.86 (t), 34.92 (d), 35.15 (t), 37.49 (t), 37.90 (t), 38.18 (d), 122.64 and 123.22 (d, C-4a and -5a), 156.02 and 160.32 (s, C-9a and -10a), 200.95 (s, C-2) (Found: C, 82.9; H, 9.1%; M^+ , 202. Calc. for $C_{14}H_{18}O$: C, 83.1; H, 9.0%; M , 202); GLC (180 °C) showed one peak, t_R 26.9 min.

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