

Cycloaddition of Acylnitroso Compounds and Nitrosobenzene with the Pyrrolidine Dienamine of Pummerer's Ketone: X-Ray Crystal Structure of a Bridged 1,2-Oxazine Derivative

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When the pyrrolidine dienamine **2** of Pummerer's ketone **1** was treated with nitrosocarbonylmethane **4**, generated *in situ* by periodate oxidation of acetohydroxamic acid, the major product was a bridged 1,2-oxazine, shown to have the structure **10** by X-ray crystallographic analysis. This structure incorporates 2 mol equiv. of nitrosocarbonylmethane with, remarkably, reductive loss of 1 nitroso oxygen, despite the oxidising reaction conditions. The same product was accompanied by a pyrrolidino enone **13** and an acetamido enone **8** when the nitroso dienophile was liberated *in situ* by retro-Diels–Alder cleavage of the corresponding 9,10-dimethylantracene cycloadduct **15**. The dienamine **2** reacted with nitrosobenzene under various conditions to afford a bridged oxazine **17** incorporating 1 mol equiv. of nitrosobenzene, a phenylamino enone **19**, and a bridged amino ketone **20** incorporating 2 equiv. of nitrosobenzene. The last two compounds had also undergone, formally, reductive loss of nitroso oxygen. However, the major product was a nitrogen-free, caged dimer **18** of the 4-oxo derivative of Pummerer's ketone.

Acylnitroso compounds XCONO (X = R, RO or RR'N), readily formed as transient intermediates by oxidation of the corresponding hydroxamic acids XCONHOH, may be trapped *in situ* as Diels–Alder adducts with conjugated dienes.¹ Yields of cycloadducts with reactive dienes are generally high. Alternatively, slow release of acylnitroso compounds by retro-Diels–Alder cleavage of the cycloadducts of 9,10-dimethylantracene^{2,3} and cyclopentadiene³ may be employed for less reactive, co-reactive dienes. The synthetic applications of acylnitroso compounds continue to receive attention.^{3,4}

Pummerer's ketone [the racemic form of **1**⁵], available in quantity as an oxidation product of *p*-cresol,⁶ has been employed⁷ as a 'pharmacophoric synthon' for the synthesis of analogues of the morphine alkaloids. We selected the derived⁸ pyrrolidine dienamine **2**† to study, as follows, the regiochemistry of cycloaddition of *C*-nitrosocarbonyl compounds RCONO with an unsymmetrical, electron-rich diene. The unexpected outcome of these studies¹⁰ (Scheme 1) then led us to explore the reaction of the dienamine **2** with nitrosobenzene (Scheme 2).

The ¹H NMR spectrum (100 MHz) of the dienamine **2**, in deuteriochloroform at ambient, spectrometer temperature (*ca.* 20 °C), showed a broad, ill-defined signal for 1-, 2-, 4- and 4a-H, in agreement with literature reports.^{8b,c} Confirmation that signal broadening arose from 'site exchange', presumably *via* the transformation **2** ⇌ **3**, was obtained from variable temperature studies. At –60 °C, a pair of AB quartets δ 6.12 and 5.74 (*J* 10 Hz, 2- and 1-H) and 5.09 and 4.40 (*J* 6 Hz, 4a- and 4-H) were observed, as expected for the dienamine structure **2**. With increasing temperature, the signals broadened and merged, reversibly, and at 60 °C had coalesced to form a broad singlet, δ 5.34. Presumably, this arose from incomplete resolution of the time-averaged signals expected at δ 5.26 [(6.12 + 4.40)/2] and 5.42 [(5.74 + 5.09)/2]. Similar, temperature-dependent effects were observed in the ¹³C spectrum. At –50 °C, the proton-decoupled spectrum showed 16 sharp signals, as expected for the structure **2**. However, signals at δ 78.6 (C-4), 89.2 (C-4a), 117.9 (C-1 or -2), and 136.9 (C-2 or -1)

had become very broad at 27 °C and had effectively disappeared at 60 °C; the other signals remained unchanged. A similar, reversible ring-opening may occur in derivatives of the dienamine **2** (see below).

The dienamine **2** reacted with nitrosocarbonylmethane **4**, formed *in situ* from acetohydroxamic acid under the usual conditions,² but gave a complex mixture of products (Scheme 1). Thus, acetohydroxamic acid (2 mol equiv.) was added to the dienamine **2** and tetraethylammonium periodate (2 mol equiv.) in dichloromethane at 0 °C. Chromatography of the reaction mixture gave some Pummerer's ketone **1**, arising by hydrolysis of the dienamine **2**, and as the major crystalline product (28%) the bridged oxazine **10**, presumably derived by hydrolysis of the corresponding enamine **9**. Many structural features of this product **10** were discerned spectroscopically. However, the molecular formula C₁₈H₂₀N₂O₅ indicated the incorporation of 2 mol equiv. of nitrosocarbonylmethane with, unexpectedly, reductive removal of 1 oxygen atom under oxidising conditions. Further, the IR spectrum showed a carbonyl band with a frequency, ν_{max}(CCl₄) 1750 cm⁻¹, higher than that expected for a comparably bridged, 6-membered ring ketone. For example, the ketone **14**, prepared from the dienamine **2** and ethyl thioacetate, showed ν_{max}(CHCl₃) 1730 cm⁻¹ (ester and ketone).¹¹ A similar oxazine (**10**; Bz replacing Ac) C₂₈H₂₄N₂O₅, also giving a high-frequency carbonyl band ν_{max}(CCl₄) 1750 cm⁻¹, was formed from the dienamine **2** and nitrosocarbonylbenzene. The structure **10** however was determined unambiguously by X-ray crystallography (see Fig. 1), and will be discussed in detail later.

Although the yield of the oxazine **10** was greater when 2 mol equiv. of acetohydroxamic acid were used rather than 1, larger quantities of this co-reactant gave yet more complex reaction mixtures without any increase in the yield of the purified product **10**. To gain insight into the mechanism of formation of the product **10**, the dienamine **2** was again treated with nitrosocarbonylmethane **4**, but this time the transient dienophile was released slowly by retro-Diels–Alder cleavage of the 9,10-dimethylantracene (DMA) cycloadduct **15**.² Thus, the dienamine **2** was heated in benzene at 60 °C with the cycloadduct **15** (2 mol equiv.) for 27 h under dry nitrogen. Again, a complex mixture of products was obtained. Chromatography on silica gave DMA (94%) and the cycloadduct **15** (7%),

† In general, *cisoid* 2-dialkylamino-1,3-dienes are not readily accessible in a pure state. For recent discussion of pyrrolidine dienamines see ref. 9 and earlier papers cited therein.

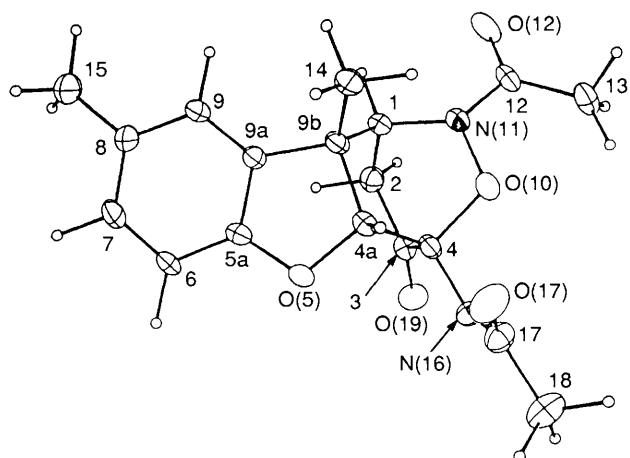
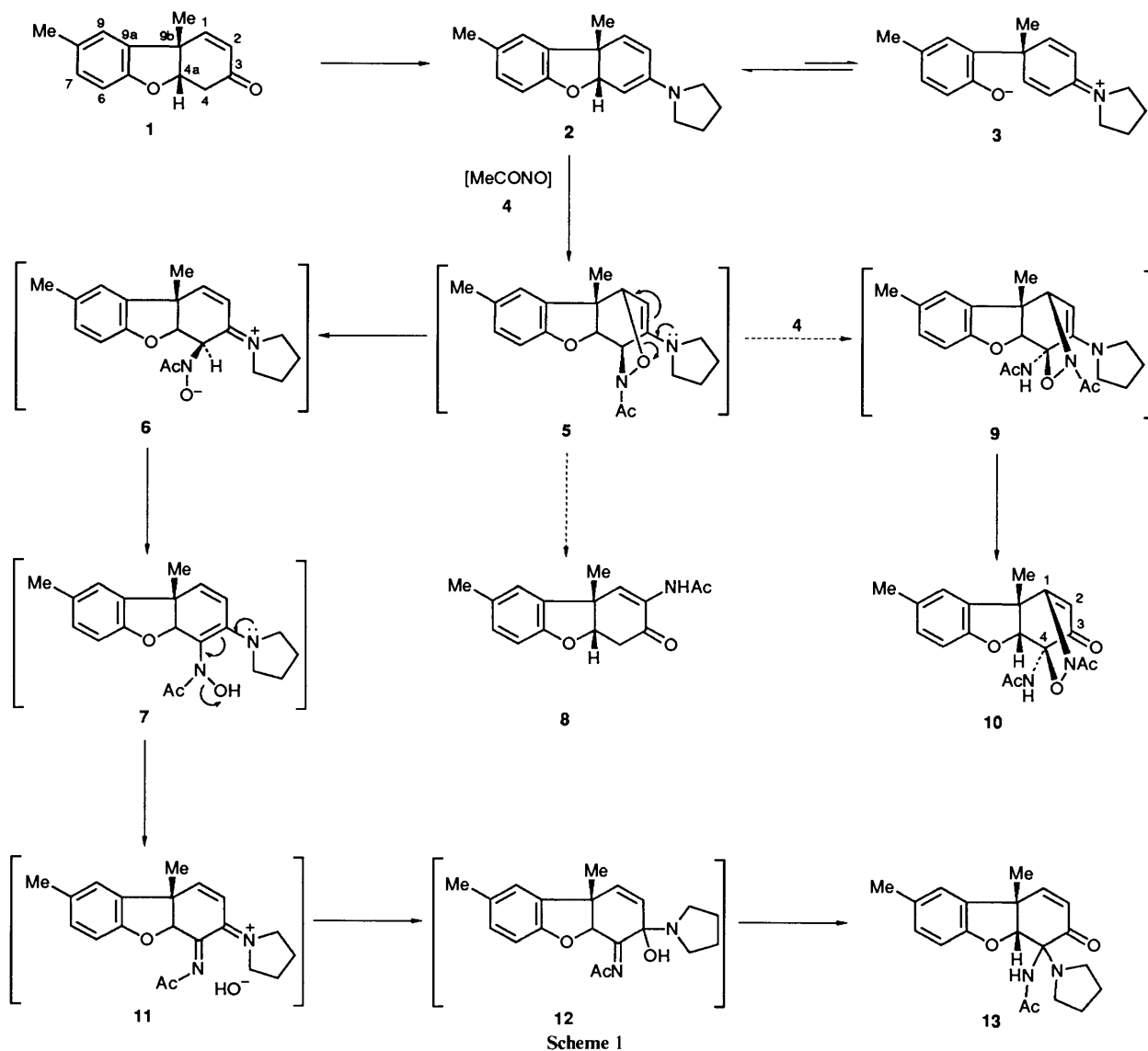
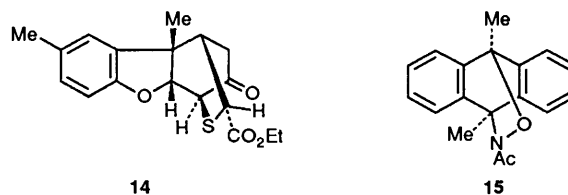


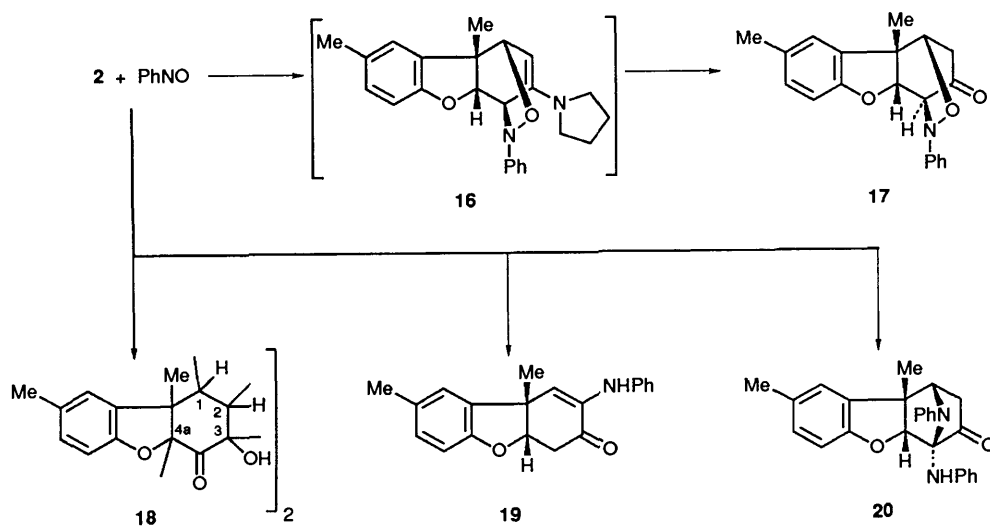
Fig. 1 X-Ray crystal structure of the bridged oxazine 10

accounting for essentially all of the latter starting material, and products derived from the dienamine 2, *viz.* Pummerer's ketone 1 (23%) [the dienamine 2 is hydrolysed on silica], the oxazine 10 (14%), and 2 new derivatives, the 4-pyrrolidino enone 13 (18%) and the 2-acetamido enone 8 (4%). Very similar results were obtained when the experiment was carried out at 70 °C for 5 h. When the dienamine 2 was treated similarly but with only 1

equiv. of the cycloadduct 15, the pyrrolidinoenone 13 (16%) and the acetamidoenone 8 (19%) were the major products (apart from DMA and Pummerer's ketone), together with very little (2%) of the oxazine 10.



Formation of the pyrrolidinoenone 13 may be accounted for plausibly by the reaction sequence 2→5→6→7→11→12→13 (Scheme 1). Initially the structure of the isomeric intermediate 7 was assigned to this product.¹⁰ However, the ¹³C spectrum showed signals for both ketonic, δ 194.0, and amidic, δ 171.3, carbonyl groups, and other spectroscopic features (see later) were more consistent with the revised constitution 13. The configuration at C(4) has not been determined. Also, attachment of the acetamido group at C(2) rather than C(4) of the enone 8 may result from opening and closure of the benzofuran ring in a dienamine⁸ [*cf.* 2 ⇌ 3] or enone^{7,12} intermediate. However, the products 8 and 10 have both unaccountably undergone reductive deoxygenation.

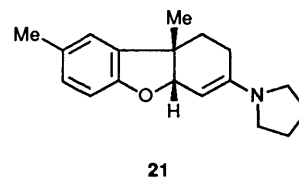


Scheme 2

In an attempt to clarify the mechanisms of the foregoing reactions, the dienamine **2** was treated with the less reactive *C*-nitroso compound, nitrosobenzene. However, complex reaction mixtures were again obtained yielding products of unexpected structure (Scheme 2). Nitrosobenzene (2 mol equiv.) in tetrachloromethane was added slowly during 30 min to the dienamine **2** in the same solvent at *ca.* -5°C . The dark mixture was chromatographed on silica, which again might have effected hydrolysis of pyrrolidine dienamine or enamine derivatives. The bridged ketone **17**, no doubt derived in this way from the simple cycloadduct **16**, was isolated in 11% yield. However, the major isolated product (42%) was, remarkably, the nitrogen-free ketone **18**, a symmetrical caged dimer of the 4-oxo derivative of Pummerer's ketone. When the dienamine **2** was added to nitrosobenzene (2 mol equiv.) under the foregoing conditions, a complex mixture was again produced but, on this occasion, a small quantity (*ca.* 3%) of a new product **19** was obtained after chromatography, along with the dimer **18** (16%). Finally, the first experiment was repeated, but with only 1 mol equiv. of nitrosobenzene, to afford the dimer **18** (42%) and a minor product **20** (*ca.* 4%) containing two phenylamino residues. A small amount of Pummerer's ketone (*ca.* 6%) was also isolated, indicating incomplete reaction of the dienamine **2**.

The chemistry of the dimer **18**, including an alternative synthesis, will be reported separately.* Here, it suffices to note that the dimer must arise *formally* by oxidation of the dienamine **2** by nitrosobenzene. Nitrosobenzene and its derivatives are known¹³ to react with 'active' methylene and methyl groups, to afford ketones and aldehydes, and aniline, after hydrolysis of the corresponding imines. The nitrogen-containing products **17**, **19** and **20** show some structural resemblance to those derived from nitrosocarbonylmethane. Once more, two of them **19** and **20** have apparently undergone reductive loss of nitroso oxygen. Interestingly, the anilinoenone **19** had been obtained previously^{8c} from the enamine **21** and nitrosobenzene; in this reaction, loss of oxygen can occur formally by dehydration, not reduction. The bridged ketone **20** might arise, like the oxazine **10**, from successive cycloadditions of two molecules of the nitroso dienophile, although this time both nitroso oxygens must be removed reductively at some stage. However, an

alternative reaction path (Scheme 3) involves aniline, a possible by-product from the formation of the dimer **18**. Ring opening of the initial cycloadduct **16** [cf. **5**→**6**] might be followed by dehydration to give the iminium ion **22** [cf. **6**→**7**→**11**]. Addition of aniline, then cyclisation, would produce the bridged ketone **20**. The intermediate **22** has the correct oxidation level to



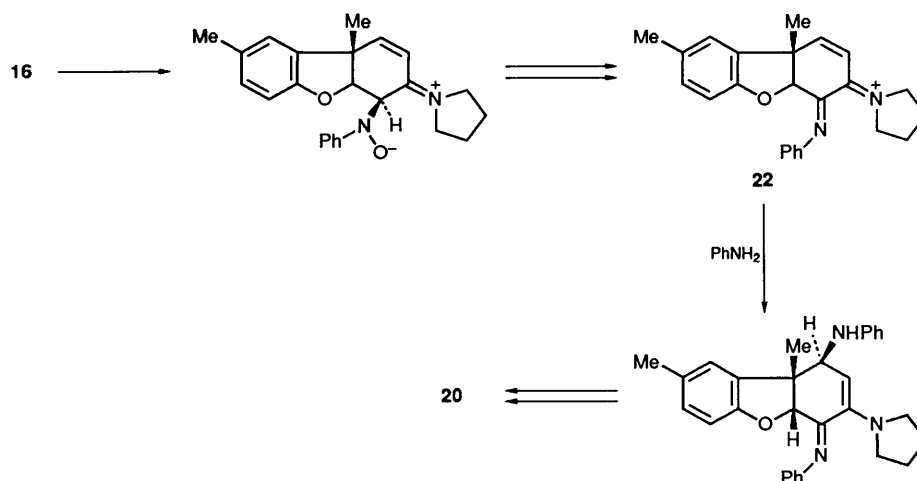
act as a precursor for the dimer **18**, with hydrolytic loss of aniline and pyrrolidine at some appropriate point. The mechanistically simplest products, **17** and **13**, obtained with nitrosobenzene and nitrosocarbonylmethane respectively, illustrate the same regiochemical preference for Diels-Alder additions to a 2-amino-1,3-diene.†

The structures of the various reaction products illustrated in Schemes 1 and 2 were determined spectroscopically, apart from those of the oxazine **10** and dimer **18**, which were obtained by X-ray crystallography. Full details are given in the Experimental section; salient features will be discussed briefly here.

The ¹H NMR spectrum of the enone **13** showed signals for a pyrrolidino group, a singlet δ 2.14 for the acetyl group, and a broad singlet δ 7.11 for an NH proton that exchanged very slowly with deuterium oxide. The presence of an unsubstituted enone system was indicated by appropriate signals in both the ¹H and ¹³C spectra. The ¹H coupling constants $J_{1,2}$ 10 and $J_{1,4a}$ 1.8 Hz were similar to those of Pummerer's ketone **1**. The olefinic proton of the enone **8** gave a lowfield signal, δ 7.44, also showing similar long-range coupling, J 1.6 Hz, with 4a-H. Therefore, the acetamido group must be attached at C(2) rather than C(1). A similar observation established the 2-phenylamino structure for the enone **19**.^{8c} The ¹H spectrum of the ketone **17**, when compared with that of the product **10**, established at once the presence of a bridged oxazine ring. However the chemical shifts for 1-H, δ 4.56 (ddd, J 3.9, 2.0 and 1.0 Hz) and 4-H, δ 4.37 (d, J 5.1 Hz), were too similar to prove

* The dimer **18** was shown by X-ray crystallography to be symmetrically linked 1-1', 2-4a', 3-3' and 4a-2', the identical monomer units being related by a 2-fold axis of symmetry. The corresponding monomer, the 4-oxo derivative of **1**, has been synthesised, as an enol, and converted into the dimer **18**.

† The cycloaddition of *C*-nitroso compounds to 1-methoxycarbonyl-1,6-dihydropyridine has been studied (ref. 14). Nitrosocarbonylmethane and -benzene add regiospecifically in the same sense; nitrosobenzene also adds regiospecifically, but in the opposite sense.



Scheme 3

unambiguously that the epoxyimino group was attached as shown **17** or with oxygen at C-4 and nitrogen at C-1. The point was settled by correlation of the ^1H and ^{13}C spectra (see Experimental section); the chemical shift, δ 78.3 for C-1 indicated attachment of oxygen, whereas the corresponding value for the oxazine **10** was only 54.2. Finally, the elemental composition of the bridged ketone **20**, $\nu_{\text{max}}(\text{CHCl}_3)$ 1757 cm^{-1} , together with the ^1H and ^{13}C spectra and evidence for one amino proton [$\nu_{\text{max}}(\text{CHCl}_3)$ 3390 cm^{-1} and δ_{H} 5.09 (br s, NH, exch. with D_2O)] established the structure as shown **20**.

X-Ray crystallographic data for the racemic, bridged oxazine **10** are given in Tables 1 and 2. Fig. 1 displays one of the two independent molecules, of opposite chirality, in the asymmetric unit, which also contains one water molecule for each pair of the oxazine. Both molecules show almost identical bond lengths and angles (Table 2). The water accounted for the micro-analytical data (C, H and N), which best fitted a hemihydrate formulation. The bonds from the nitrogen atom of the *N*-acetyloxazine ring were almost co-planar, the sum of the angles (the numbering of Fig. 1 is used here) O(10)–N(11)–C(12), C(1)–N(11)–C(12) and C(1)–N(11)–O(10) being 356.6° for molecule A and 357.9° for molecule B. The O(10)–N(11)–C(12)–C(13) torsion angles, 6.2 and 4.1° for molecules A and B, respectively, also indicated extensive conjugation in this *N*-acetyl group. Likewise, the 4-acetamido group had the usual planar, *trans* stereochemistry. There was therefore no reason to assign the high frequency IR band, 1750 cm^{-1} , to either of the amidic carbonyl groups. However, the ketonic carbonyl group appeared to form an intramolecular hydrogen-bond with the 4-acetamido group; O(19) \cdots N(16), $2.668(12) \text{ \AA}$ with O(19) \cdots H(N), $2.19(4) \text{ \AA}$ for molecule A, and $2.704(12) \text{ \AA}$ and $2.31(5) \text{ \AA}$ for molecule B. This hydrogen-bonding would normally be expected to lower the stretching frequency of the keto group. Consequently, the reason for the high frequency of the 1750 cm^{-1} band of the oxazine **10**, and of the corresponding *N*-benzoyl derivative, is not clear, although the presence of two electronegative atoms α to the keto group may be significant. It was noticed that the sharp 1750 cm^{-1} band was substantially weaker than the sharp band at 1708 cm^{-1} and the broad band at 1665 cm^{-1} , attributed to the C(12)=O and C(17)=O carbonyl groups, respectively. The water molecule of the hemihydrate appears not to be involved in hydrogen bonding with either oxazine molecule, having a sole contact distance of $2.887(1) \text{ \AA}$ with a neighbouring water molecule.

Experimental

M.p.s were determined with a Kofler hot-stage apparatus.

Table 1 Fractional atomic co-ordinates for compound **10** with esds in parentheses

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
O(5)	–0.7832(8)	–0.5944(7)	–0.7284(5)
O(10)	–0.8842(9)	–0.3533(7)	–0.9049(5)
O(12)	–0.7425(11)	–0.0987(8)	–0.9472(5)
O(17)	–0.9068(11)	–0.6096(10)	–0.9171(7)
O(19)	–1.0688(9)	–0.3591(8)	–0.7145(5)
O(5')	–0.1301(8)	–0.0578(7)	–0.8038(4)
O(10')	–0.5136(8)	–0.0507(7)	–0.7549(4)
O(12')	–0.6332(10)	–0.0710(9)	–0.5416(5)
O(17')	–0.3403(11)	–0.2568(8)	–0.8352(5)
O(19')	–0.3986(11)	0.1801(8)	–0.8828(5)
O(100)	–0.9381(7)	–0.3953(7)	–0.5286(4)
N(11)	–0.7902(11)	–0.2797(10)	–0.9015(6)
N(16)	–1.0218(10)	–0.4885(8)	–0.8290(6)
N(11')	–0.5325(10)	–0.0247(9)	–0.6749(6)
N(16')	–0.3673(10)	–0.0555(8)	–0.8806(5)
C(1)	–0.7246(12)	–0.3202(11)	–0.8276(7)
C(2)	–0.8437(13)	–0.2998(10)	–0.7552(7)
C(3)	–0.9536(13)	–0.3653(10)	–0.7583(7)
C(4)	–0.9082(12)	–0.4385(10)	–0.8241(6)
C(4A)	–0.7673(12)	–0.5233(10)	–0.8134(6)
C(5A)	–0.6776(12)	–0.5856(10)	–0.6919(7)
C(6)	–0.6488(14)	–0.6520(11)	–0.6149(7)
C(7)	–0.5351(15)	–0.6357(12)	–0.5880(7)
C(8)	–0.4514(14)	–0.5550(13)	–0.6347(8)
C(9)	–0.4849(12)	–0.4884(11)	–0.7118(7)
C(9A)	–0.5964(12)	–0.5057(10)	–0.7413(6)
C(9B)	–0.6517(12)	–0.4504(10)	–0.8220(6)
C(12)	–0.8103(14)	–0.1693(12)	–0.9518(7)
C(13)	–0.9136(15)	–0.1445(11)	–1.0087(7)
C(14)	–0.5388(13)	–0.4670(12)	–0.8971(7)
C(15)	–0.3304(17)	–0.5367(16)	–0.6032(9)
C(17)	–1.0143(15)	–0.5652(13)	–0.8769(8)
C(18)	–1.1520(15)	–0.5959(15)	–0.8742(10)
C(1')	–0.4304(12)	0.0392(10)	–0.6648(7)
C(2')	–0.4398(13)	0.1515(10)	–0.7352(7)
C(3')	–0.4035(12)	0.1106(11)	–0.8152(7)
C(4')	–0.3799(11)	–0.0239(10)	–0.8046(7)
C(4A')	–0.2618(11)	–0.0891(10)	–0.7550(6)
C(5A')	–0.0815(12)	0.0051(10)	–0.7618(6)
C(6')	0.0402(13)	0.0499(12)	–0.7908(7)
C(7')	0.0753(13)	0.1077(12)	–0.7401(8)
C(8')	–0.0035(14)	0.1204(12)	–0.6634(8)
C(9')	–0.1264(13)	0.0738(12)	–0.6366(7)
C(9A')	–0.1640(12)	0.0167(10)	–0.6861(6)
C(9B')	–0.2854(12)	–0.0453(9)	–0.6719(6)
C(12')	–0.6187(13)	–0.0880(12)	–0.6128(8)
C(13')	–0.6873(15)	–0.1665(13)	–0.6373(8)
C(14')	–0.2720(13)	–0.1530(10)	–0.5960(6)
C(15')	0.0427(16)	0.1789(15)	–0.6085(9)
C(17')	–0.3470(13)	–0.1682(12)	–0.8926(7)
C(18')	–0.3355(14)	–0.1779(11)	–0.9807(7)

Table 2 Bond lengths (Å) and bond angles (°) for compound **10** with esds in parentheses

	Mol A	Mol (B')
(a) Bond lengths		
O(5)–C(4A)	1.462(13)	1.462(13)
O(5)–C(5A)	1.364(13)	1.382(13)
O(10)–N(11)	1.447(13)	1.432(12)
O(10)–C(4)	1.482(14)	1.465(14)
O(12)–C(12)	1.224(16)	1.247(16)
O(17)–C(17)	1.203(18)	1.224(16)
O(19)–C(3)	1.212(16)	1.219(16)
N(11)–C(1)	1.449(15)	1.470(15)
N(11)–C(12)	1.346(17)	1.385(17)
N(16)–C(4)	1.426(14)	1.406(13)
N(16)–C(17)	1.346(16)	1.353(17)
C(1)–C(2)	1.525(17)	1.526(17)
C(1)–C(9B)	1.502(17)	1.516(17)
C(2)–C(3)	1.506(16)	1.499(17)
C(3)–C(4)	1.511(16)	1.508(17)
C(4)–C(4A)	1.501(17)	1.511(15)
C(4A)–C(9B)	1.564(16)	1.578(14)
C(5A)–C(6)	1.380(16)	1.380(17)
C(5A)–C(9A)	1.386(16)	1.381(16)
C(6)–C(7)	1.377(18)	1.377(17)
C(7)–C(8)	1.39(2)	1.39(2)
C(8)–C(9)	1.395(18)	1.401(18)
C(8)–C(15)	1.497(19)	1.499(19)
C(9)–C(9A)	1.386(15)	1.366(15)
C(9A)–C(9B)	1.506(15)	1.508(15)
C(9B)–C(14)	1.517(17)	1.511(15)
C(12)–C(13)	1.479(18)	1.465(19)
C(17)–C(18)	1.49(2)	1.507(16)
(b) Bond angles		
C(4A)–O(5)–C(5A)	108.1(9)	108.3(8)
N(11)–O(10)–C(4)	110.1(8)	110.4(8)
O(10)–N(11)–C(1)	113.5(9)	115.2(9)
O(10)–N(11)–C(12)	114.8(10)	115.4(10)
C(1)–N(11)–C(12)	128.3(11)	127.2(10)
C(4)–N(16)–C(17)	125.6(10)	126.4(10)
N(11)–C(1)–C(2)	106.5(10)	105.2(9)
N(11)–C(1)–C(9B)	107.5(10)	107.1(9)
C(2)–C(1)–C(9B)	113.2(10)	112.5(9)
C(1)–C(2)–C(3)	106.9(10)	107.7(10)
O(19)–C(3)–C(2)	124.6(11)	123.1(11)
O(19)–C(3)–C(4)	122.3(11)	123.0(11)
C(2)–C(3)–C(4)	113.1(10)	113.9(10)
O(10)–C(4)–N(16)	105.2(9)	106.7(9)
O(10)–C(4)–C(3)	107.1(9)	103.1(9)
O(10)–C(4)–C(4A)	106.0(9)	108.2(9)
N(16)–C(4)–C(3)	110.1(10)	111.5(10)
N(16)–C(4)–C(4A)	117.5(10)	115.7(9)
C(3)–C(4)–C(4A)	110.2(10)	110.8(9)
O(5)–C(4A)–C(4)	106.6(9)	107.7(8)
O(5)–C(4A)–C(9B)	107.0(8)	106.6(8)
C(4)–C(4A)–C(9B)	110.0(9)	111.4(9)
O(5)–C(5A)–C(6)	124.4(11)	123.7(10)
O(5)–C(5A)–C(9A)	113.3(10)	113.7(10)
C(6)–C(5A)–C(9A)	122.2(11)	122.5(11)
C(5A)–C(6)–C(7)	117.3(12)	116.2(11)
C(6)–C(7)–C(8)	122.7(12)	123.3(12)
C(7)–C(8)–C(9)	118.3(12)	118.5(12)
C(7)–C(8)–C(15)	121.7(12)	121.3(12)
C(9)–C(8)–C(15)	120.0(12)	120.1(12)
C(8)–C(9)–C(9A)	120.1(11)	119.4(11)
C(5A)–C(9A)–C(9)	119.3(10)	120.2(11)
C(5A)–C(9A)–C(9B)	109.5(10)	109.2(10)
C(9)–C(9A)–C(9B)	131.2(10)	130.6(10)
C(1)–C(9B)–C(4A)	108.0(9)	107.0(9)
C(1)–C(9B)–C(9A)	111.6(9)	113.6(9)
C(1)–C(9B)–C(14)	111.4(10)	112.3(9)
C(4A)–C(9B)–C(9A)	101.2(9)	102.1(8)
C(4A)–C(9B)–C(14)	111.0(10)	111.6(9)
C(9A)–C(9B)–C(14)	113.0(10)	109.8(9)
O(12)–C(12)–N(11)	118.2(12)	117.1(12)
O(12)–C(12)–C(13)	125.7(12)	126.1(12)

Table 2 (continued)

	Mol A	Mol (B')
(b) Bond angles		
N(12)–C(12)–C(13)	116.1(12)	116.8(12)
O(17)–C(17)–N(16)	124.6(13)	122.1(11)
O(17)–C(17)–C(18)	121.3(14)	121.9(12)
N(16)–C(17)–C(18)	114.0(12)	116.0(11)

NMR spectra were recorded for deuteriochloroform solutions. Light petroleum refers to the fraction b.p. 40–60 °C and solutions in organic solvents were dried with magnesium sulphate and evaporated under reduced pressure. Mass spectra were obtained by electron impact at 70 eV.

The Pyrrolidine Dienamine 2.—This derivative was prepared by heating Pummerer's ketone and pyrrolidine in benzene or toluene as described before.^{8b,c} When methanol was used as solvent, as recommended,^{8a} the resulting dienamine **2** was contaminated with variable amounts of a methanol adduct (probably the 1β-methoxy-1,2-dihydro derivative⁷). The dienamine **2** gave δ_{H} (100 MHz; 293 K) 1.38 (s, 9b-Me), 1.89 (m, NCH₂CH₂), 2.30 (s, 8-Me), 3.25 (m, NCH₂CH₂), 5.0–5.8 (br s, 1-, 2-, 4- and 4a-H), 6.65 (d, J 8, 6-H), 6.86 (br d, J 8, 7-H) and 6.98 (br s, 9-H); see the main text for δ_{H} values at 213 K; δ_{C} (50.3 MHz; at 223 K) 20.9 (8-Me), 22.1 (9b-Me), 25.1 (2 × NCH₂CH₂), 43.4 (C-9b), 46.9 (2 × NCH₂CH₂), 78.6* (C-4), 89.2* (C-4a), 109.0 (C-6), 117.9* (C-1 or -2), 123.7 (C-9), 127.5 (C-7), 129.5 (C-8 or -9a), 133.6 (C-9a or -8), 136.8* (C-2 or -1), 143.1 (C-3) and 156.7 (C-5a); asterisked signals were very broad at 300 K and were undetectable at 333 K, but other signals remain unchanged.

Reaction of the Dienamine 2 with Nitrosocarbonylmethane 4 Generated from Acetohydroxamic Acid: the Oxazine 10.—The dienamine **2** (1.29 g, 4.83 mmol) and tetraethylammonium periodate (3.10 g, 9.66 mmol) (see the CAUTIONARY note in ref. 2 concerning the preparation of this salt) were stirred at 0 °C in dry dichloromethane (30 ml). Acetohydroxamic acid (720 mg, 9.6 mmol) was added in small portions during 10 min. After 1 h, the mixture was washed successively with aqueous sodium thiosulphate and water and then dried and evaporated. The residue was chromatographed on silica plates developed with ethyl acetate–light petroleum (3:1). Elution of a band at R_{f} 0.34 gave 4α-acetamido-1,2,3,4,4aβ,9b-hexahydro-8,9bβ-dimethyl-1β,4β-(N-acetylepoxymino)dibenzofuran-3-one **10** (0.37 g, 22%), m.p. 192–193 °C (from dichloromethane–light petroleum) (Found: C, 61.1; H, 5.9; N, 7.9. C₁₈H₂₀N₂O₅·0.5H₂O requires C, 61.2; H, 5.9; N, 7.9%); ν_{max} (CCl₄)/cm⁻¹ 3380, 1750, 1708 and 1665; λ_{max} (MeOH)/nm 224sh (ϵ 13 800 dm³ mol⁻¹ cm⁻¹) and 292 (3900); δ_{H} (200 MHz) 1.65 (s, 9b-Me), 2.13 (s, ONAc), 2.15 (s, NHAc), 2.26 (s, 8-Me), 2.32 (dd, J 19.5 and 1.9, 2-H), 2.70 (dd, J 19.5 and 3.9, 2-H), 5.10 (br dd, J ca. 4 and 2 with fine splitting, 1-H), 5.98 (s, 4a-H), 6.63 (d, J 8.2, 6-H), 6.85 (br s, NH, exch. with D₂O), 6.90 (m, 9-H) and 6.95 (dm, J 8.2, 7-H), the signal at δ 2.15 was identified as that of the NHAc group from an NOE enhancement (4.2%) when the NH signal was irradiated and vice versa (5.0%); δ_{C} (50.4 MHz) 20.2 (9b-Me), 20.75 (8-Me), 24.3 (COMe), 24.5 (COMe), 39.1 (C-2), 49.0 (C-9b), 54.2 (C-1), 83.5 (C-4a), 86.0 (C-4), 110.2 (C-6), 123.7 (C-9), 129.6 (C-8 or -9a), 130.5 (C-7), 131.9 (C-9a or -8), 156.3 (C-5a), 169.5 (COMe), 170.3 (COMe) and 197.45(C-3); m/z 344.1392. C₁₈H₂₀N₂O₅ requires M , 344.1372.

X-Ray Crystal Structure Analysis of the Bridged Oxazine 10.—Crystal data. C₁₈H₂₀N₂O₅·0.5H₂O, M = 353.4, Triclinic, a = 9.890(1), b = 11.789(2), c = 16.969(4) Å, α = 74.63(2),

$\beta = 77.33(2)$, $\gamma = 74.74(1)^\circ$, $U = 1816.5 \text{ \AA}^3$, $F(000) = 728$, $D_c = 1.29 \text{ g cm}^{-3}$, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 0.95 \text{ cm}^{-1}$, systematic absences – none; space group $P\bar{1}(C_1^1)$.

Crystallographic measurements. Cell dimensions were derived by least-squares treatment of the setting angles of 25 reflections measured on an Enraf-Nonius CAD-4 diffractometer with Mo-K α radiation. 5690 Independent intensities were collected in the range $\theta \leq 24^\circ$ and of these 2428 satisfied the criterion $I \geq 3.0\sigma(I)$.

Structure analysis. The crystal structure was solved using the direct phasing procedure MITHRIL.¹⁵ Refinement with anisotropic thermal parameters for the C, N and O atoms converged at R 0.087, R_w 0.104 with weights $W \propto 1/\sigma^2(F)$. H-atom co-ordinates were calculated and included, but not refined, in the final cycles of least-squares. Fourier, least-squares, geometry and ORTEP calculations were performed with the GX system of programs.¹⁶

Atomic co-ordinates are listed in Table 1, and bond lengths and angles in Table 2.

Reaction of the Dienamine 2 with Nitrosocarbonylbenzene; the N-Benzoyloxazine (10; Bz replacing Ac).—Benzohydroxamic acid (634 mg, 4.62 mmol) was added in small portions with stirring during 15 min to the dienamine **2** (1.23 g, 4.61 mmol) and tetraethylammonium periodate (1.48 g, 4.61 mmol) in dichloromethane (30 ml) at 0°C . The reaction products were isolated and chromatographed, as described for the acetyl derivative **10**, to give 4*x*-benzamido-1,2,3,4,4a β ,9b-hexahydro-8,9b β -dimethyl-1 β ,4 β -(N-benzoyloxyimino)dibenzofuran-3-one [0.19 g, 18% (based upon BzNH₂O)], m.p. 186–188 $^\circ\text{C}$ (from dichloromethane–light petroleum) (Found: C, 71.85; H, 5.4; N, 5.9. $\text{C}_{28}\text{H}_{24}\text{N}_2\text{O}_5$ requires C, 71.8; H, 5.1; N, 6.0%; $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$ 3385, 1750, 1688 and 1640; $\delta(90 \text{ MHz})$ 1.84 (s, 9b-Me), 2.28 (s, 8-Me), 2.42 (dd, J 19 and ca. 2, 2-H), 2.94 (dd, J 19 and ca. 4, 2-H), 5.28 (m, 1-H), 6.31 (s, 4a-H), 6.63 (d, J 8, 6-H), 6.98 (m, 7- and 9-H), 7.45 (m, *m*- and *p*-Bz-H) and 7.86 (m, *o*-Bz-H); m/z 468.1692. $\text{C}_{28}\text{H}_{24}\text{N}_2\text{O}_5$ requires M , 468.1685. Equimolecular amounts of co-reactants were employed in this preparation before the composition of the product had been established; the use of 2 mol equiv. of benzohydroxamic acid and the oxidant is suggested for any future preparation of (**10**; Bz replacing Ac) (*cf.* the foregoing preparation of **10**).

Reaction of the Dienamine 2 with the Cycloadduct 15 of Nitrosocarbonylmethane 4; the Pyrrolidinoenone 13 and the Acetamido Enone 8.—The cycloadduct **15** (2.23 g, 8 mmol) of 9,10-dimethylantracene (DMA) and nitrosocarbonylmethane **4** and the dienamine **2** (1.07 g, 4 mmol) were heated in benzene (50 ml) under oxygen-free, dry nitrogen at 60°C for 27 h. The mixture was evaporated and the residue was chromatographed on a column of silica HF₂₅₄. Elution with hexane–ethyl acetate (10:1) gave successively DMA (1.55 g, 7.52 mmol, 94%), the cycloadduct **15** (0.15 g, 0.54 mmol, 7%), Pummerer's ketone **1** (0.20 g, 0.93 mmol, 23%), and the pyrrolidinoenone **13** (0.24 g, 0.71 mmol, 18%). Further elution, with hexane–ethyl acetate (1:1), gave successively the acetamido enone **8** (40 mg, 0.15 mmol, 4%) and the oxazine **10** (0.20 g, 0.58 mmol, 14%). 4-Acetamido-4a β ,9b β -dihydro-8,9b β -dimethyl-4-(pyrrolidin-1-yl)-dibenzofuran-3(4H)-one **13** had m.p. 166–168 $^\circ\text{C}$ (from diethyl ether–light petroleum) (Found: C, 70.6; H, 7.35; N, 8.3. $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_3$ requires C, 70.6; H, 7.1; N, 8.2%; $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$ 3385, 1678 and 1488; $\delta_{\text{H}}(100 \text{ MHz})$ 1.68 (m, 9b-Me and $2 \times \text{NCH}_2\text{CH}_2$), 2.14 (s, NAc), 2.28 (s, 8-Me), 2.52 and 2.78 ($2 \times$ m, $2 \times \text{NCH}_2\text{CH}_2$), 5.83 (d, J 10, 2-H), 6.00 (d, J 1.8, 4a-H), 6.40 (dd, J 10 and 1.8, 1-H), 6.64 (d, J 8.4, 6-H), 6.92 (m, 7- and 9-H) and 7.11 (br s, NH, v. slow exch. with D_2O); $\delta_{\text{C}}(50.3 \text{ MHz})$ 20.8 (8-Me), 21.7 (9b-Me),

23.0 ($2 \times \text{NCH}_2\text{CH}_2$), 24.6 (COMe), 47.2 (9b-C), 47.4 ($2 \times \text{NCH}_2\text{CH}_2$), 74.8 (C-4), 85.3 (C-4a), 110.5 (C-6), 120.6 (C-2), 122.8 (C-9), 129.7 (C-7), 130.6 (C-8 or -9a), 132.4 (C-9a or -8), 150.7 (C-1), 155.9 (C-5a), 171.3 (COMe) and 194.0 (C-3); m/z 340 (M^{+}).

2-Acetamido-4a β ,9b β -dihydro-8,9b β -dimethyldibenzofuran-3(4H)-one **8** had m.p. 167–168 $^\circ\text{C}$ (from diethyl ether–light petroleum) (Found: C, 70.0; H, 6.3; N, 5.0. $\text{C}_{16}\text{H}_{17}\text{NO}_3$ requires C, 70.85; H, 6.3; N, 5.2%; $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$ 3385, 1675 and 1510 cm^{-1} ; $\delta_{\text{H}}(100 \text{ MHz})$ 1.60 (s, 9b-Me), 2.04 (s, Ac), 2.30 (s, 8-Me), 2.86 (dd, J 17.7 and 3.7, 4-H), 3.16 (dd, J 17.7 and 2.9, 4-H), 4.58 (ddd, J 3.7, 2.9 and 1.7, 4a-H), 6.68 (d, J 8.0, 6-H), 6.95 (br d, J 8.0, 7-H), 7.05 (br s, 9-H), 7.44 (d, J 1.7, 1-H) and 7.73 (br s, NH, exch. with D_2O); m/z 271 (M^{+}).

The foregoing experiment was repeated, but at 70°C for 5 h, to afford DMA (94%), the cycloadduct **15** (8%), Pummerer's ketone **1** (17%), the pyrrolidinoenone **13** (16%), the acetamidoenone **8** (6%), and the oxazine **10** (13%). Finally, equimolecular amounts of the dienamine **2** and the cycloadduct **15** were heated in benzene at 70°C for 5 h to yield DMA (94%), Pummerer's ketone (25%), the pyrrolidino enone **13** (16%), the acetamido enone **8** (19%) and the oxazine **10** (2%).

Reaction of the Dienamine 2 with Nitrosobenzene.—(a) *Characterisation of the bridged oxazine 17 and the symmetrical dimer 18.*—Nitrosobenzene (0.882 g, 8.24 mmol) in tetrachloromethane (20 ml) was added dropwise with stirring during 30 min to the dienamine **2** (1.10 g, 4.12 mmol) in tetrachloromethane (25 ml) at -5°C . The dark, red-brown mixture was evaporated and the residue chromatographed on a column of silica HF₂₅₄. Elution with benzene gave 1,2,4a β ,9b β -tetrahydro-8,9b β -dimethyl-1 β ,4 β -(N-phenylepoxyimino)dibenzofuran-3(4H)-one **17** (0.14 g, 11%), m.p. 154–156 $^\circ\text{C}$ (from hexane) (Found: C, 75.0; H, 6.7; N, 4.6. $\text{C}_{20}\text{H}_{19}\text{NO}_3$ requires C, 74.8; H, 5.9; N, 4.4%; $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$ 1742; $\delta_{\text{H}}(200 \text{ MHz})$ 1.77 (s, 9b-Me), 2.24 (dd, J 19.3 and 2.0, 2-H), 2.27 (s, 8-Me), 2.48 (dd, J 19.3 and 3.9, 2-H), 4.37 (d, J 5.1, 4-H), 4.56 (ddd, J 3.9, 2.0 and 1.0, 1-H), 5.09 (dd, J 5.0 and 1.0, 4a-H), 6.68 (d, J 8.1, 6-H), 6.84 (m, 9-H), 6.96 (dm, J ca. 9, 7-H), 6.98 (m, *p*-Ph-H), 7.09 (dm, J 9.0, *o*-Ph-H) and 7.28 (tm, J 9, *m*-Ph-H); $\delta_{\text{C}}(50.4 \text{ MHz})$ 20.8 (8-Me), 24.8 (9b-Me), 41.6 (C-2), 48.7 (C-9b), 67.0 (C-4), 78.3 (C-1), 86.7 (C-4a), 110.1 (C-6), 115.9 (*o*-Ph-C), 123.1 (*p*-Ph-C), 123.6 (C-9), 129.1 (*m*-Ph-C), 130.0 (C-8 or -9a), 130.1 (C-7), 131.2 (C-9a or -8), 149.6 (*ipso*-Ph-C), 157.1 (C-5a) and 201.8 (C-3); a direct C–H shift correlation was observed, *inter alia*, between δ_{H} 4.56 and δ_{C} 78.3; m/z 321 (M^{+}). Elution with benzene–ethyl acetate (9:1) then gave the symmetrical dimer **18** (0.40 g, 42%), m.p. $>310^\circ\text{C}$ (decomp.) (from benzene or dichloromethane–light petroleum) (Found: C, 76.0; H, 5.9. $\text{C}_{28}\text{H}_{24}\text{O}_6 \cdot \text{C}_6\text{H}_6$ requires C, 76.4; H, 5.6%; $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$ 3530 and 1772; $\delta_{\text{H}}(200 \text{ MHz})$ 1.05 (s, 9b-Me), 2.33 (s, 8-Me), 2.93 and 3.09 (AA'BB' octet, J_{AB} 5.45, J_{AB} 2.35, J_{AA} 3.15 and J_{BB} ca. 0, 1- and 2-H), 3.68 (br s, OH, exch. with D_2O), 6.87 (d, J 8.0, 6-H), 6.88 (m, 9-H), 7.03 (dm, J 8.0, 7-H) and 7.35 (PhH); $\delta_{\text{C}}(50.4 \text{ MHz})$ 20.3 (9b-Me), 21.0 (8-Me), 54.4 (C-1), 62.3 (C-2), 63.7 (C-9b), 87.6 (C-3), 96.1 (C-4a), 111.5 (C-6), 123.3 (C-9), 128.3 (C_6H_6), 130.0 (C-7), 132.0 (C-8 or -9a), 132.5 (C-9a or -8), 156.8 (C-5a) and 201.9 (C-4); m/z 456.1576. $\text{C}_{28}\text{H}_{24}\text{O}_6$ requires M , 456.1573.

(b) *Characterisation of the anilinoenone 19.* The foregoing experiment was repeated but with slow addition of the dienamine in tetrachloromethane to nitrosobenzene (2 mol equiv.) in the same solvent. Chromatography of the product mixture on silica and elution with benzene gave 2-anilino-4a β ,9a-dihydro-8,9b β -dimethyldibenzofuran-3(4H)-one **19** (3%), m.p. 185–186 $^\circ\text{C}$ (from dichloromethane–light petroleum) (lit.^{8c} 182–184 $^\circ\text{C}$) (Found: C, 78.1; H, 6.1; N, 4.7. Calc. for $\text{C}_{20}\text{H}_{19}\text{NO}_2$: C, 78.7; H, 6.2; N, 4.6%; $\nu_{\text{max}}(\text{CCl}_4)/\text{cm}^{-1}$ 3380

and 1685; δ_{H} (200 MHz) 1.59 (s, 9b-Me), 2.31 (s, 8-Me), 2.95 (dd, J 17.7 and 3.8, 4-H), 3.20 (dd, J 17.7 and 3.0, 4-H), 4.61 (ddd, J 3.8, 3.0 and 1.7, 4a-H), 5.88 (d, J 1.6, 1-H), 6.28 (br s, NH, exch. with D_2O), 6.72 (d, J 8, 6-H), 6.90 (m, 7-, 9- and *o*- and *p*-Ph-H) and 7.20 (m, *m*-Ph-H); δ_{C} (50.4 MHz) 20.9 (8-Me), 23.1 (9b-Me), 37.1 (C-4), 44.7 (C-9b), 85.7 (C-4a), 109.9 (C-6), 116.3 (*p*-Ph-C), 119.2 (*o*-Ph-C), 121.5 (C-1), 122.7 (C-9), 129.0 (C-7), 129.2 (*m*-Ph-H), 131.0 and 133.0 (C-8 and -9a), 134.4 (C-2), 141.2 (*ipso*-Ph-C), 156.4 (C-5a) and 191.4 (C-3); m/z 305. Elution with benzene-ethyl acetate (9:1) then gave the dimer **18** (16%).

(c) *Characterisation of the epiphenylimino derivative 20*. The first experiment was repeated but with addition of nitrosobenzene to an equimolecular amount of the dienamine **2**. Chromatography gave 4-anilino-1,2,4a β ,9b-tetrahydro-8,9b β -dimethyl-1 β ,4 β -(*N*-phenylepimino)dibenzofuran-3(4H)-one **20** (4%), m.p. 195–196 °C (from dichloromethane-light petroleum) (Found: C, 78.5; H, 6.1; N, 7.2. $\text{C}_{26}\text{H}_{24}\text{N}_2\text{O}_2$ requires C, 78.8; H, 6.1; N, 7.1%); ν_{max} (CHCl_3)/ cm^{-1} 3390 and 1757; δ_{H} (200 MHz) 1.82 (d, J 18.6, 2-H), 1.88 (s, 9b-Me), 2.30 (s, 8-Me), 2.34 (ddd, J 18.6, 5.7 and 0.5, 2-H), 4.22 (dd, J 5.7 and 1.8, 1-H), 5.09 (br s, NH exch. with D_2O), 5.38 (d, J 1.8, 4a-H), 6.63 (d, J 8.8, 6-H), 6.82–7.00 (m, 9- and *o*-Ph-H), 7.00–7.10 (m, 7- and *p*-Ph-H) and 7.13–7.31 (m, *m*-Ph-H); δ_{C} (50.4 MHz) 20.8 (8-Me), 24.6 (9b-Me), 35.7 (C-2), 51.5 (C-9b), 64.8 (C-1), 86.8 (C-4a), 86.9 (C-4), 110.1 (C-6), 116.3 and 120.1 (*o*-Ph-C), 119.8 and 122.2 (*p*-Ph-C), 123.8 (C-9), 129.1 and 129.4 (*m*-Ph-C), 130.0 (C-7), 130.2 and 131.0 (C-8 and -9a), 142.5 and 144.2 (*ipso*-Ph-C), 158.3 (C-5a) and 204.9 (C-3); m/z 396.1828. $\text{C}_{26}\text{H}_{24}\text{N}_2\text{O}_2$ requires M , 396.1837. The dimer **18** (42%) was also isolated, along with Pummerer's ketone **1** (6%).

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