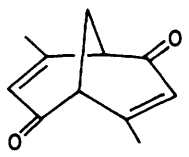
Reactions of 4,8-Dimethylbicyclo[3.3.1]nona-3,7-diene-2,6-dione and of 4,6-Dimethylbicyclo[3.3.1]nona-3,6-diene-2,8-dione with Hydroxylamine and with Hydrazines

John M. Mellor,* Ranjith Pathirana, and John H. A. Stibbard
Department of Chemistry, The University, Southampton SO9 5NH

Hydrazine reacts with 4,8-dimethylbicyclo[3.3.1]nona-3,7-diene-2,6-dione by condensation and Michael-type addition to give 4,9-dimethyl-2,3,7,8-tetra-azatetracyclo[7.3.1.0.^{4,12}0^{6,10}]trideca-1,6-diene, but hydroxylamine and other hydrazine derivatives only give bicyclic condensation products. Beckmann rearrangement of the oximes of 4,8-dimethylbicyclo[3.3.1]nona-3,7-diene-2,6-dione and of 4,6-dimethylbicyclo[3.3.1]nona-3,6-diene-2,8-dione gives 2-azabicyclo[4.3.1]decadienediones.

Knoevenagel [1] has described the acid-catalysed cyclisation of polyketones to give bicyclo[3.3.1]nona-3,7-diene-2,6-diones and bicyclo[3.3.1]nona-2,8-diones and briefly notes the failure to characterize 4,8-dimethylbicyclo[3.3.1]nona-3,7-diene-2,6-dione (1) by reaction with hydroxylamine. Reaction might have been expected to lead to mono- and di-oximes, or possibly by further addition to the activated carbon–carbon double bonds to tricyclic and tetracyclic products. Similarly, hydrazines might give mono- or bis-hydrazones or by analogous addition tricyclic and tetracyclic products. Such tricyclic or tetracyclic products [*e.g.* (2) and (3) by reaction with hydrazine] are characterised by the incorporation of the carbon–nitrogen double bond at a bridgehead (anti-Bredt) position. In view of the current interest in the synthesis and chemistry of alkenes [2] and imines [3,4] having a double bond at a bridgehead position, we now report our investigations into the synthesis of the first examples of oximes and hydrazones having such double bonds. In this paper we report the synthesis of the bishydrazone (3) and the synthesis and chemistry of oxime products from (1) and the related (4). In the following paper [5] we report the unusual ring cleavage reactions of the bishydrazone (3).

Reaction of compound (1) with hydrazine hydrate in ethanol affords quantitatively on removal of solvent a white crystalline bishydrazone (3). The tetracyclic nature of (3) is indicated by the absence of signals associated with vinyl protons in the ^{1}H n.m.r. spectrum and the related absence of signals associated with vinyl carbons in the ^{13}C n.m.r. spectrum. Observation of only six resonances in the latter spectrum requires a symmetrical structure and cyclisation is indicated by the resonance at 76.18 p.p.m. associated with a quaternary carbon centre. Further spectroscopic data (see Experimental section) are fully consistent with the assigned structure. An alternative mode of cyclisation is possible. Instead of cyclisation to give the bishydrazone (3) in which the imine double bonds are contained at the bridgehead position in a bicyclo[5.2.1]decene framework, there might be cyclisation to give compound (5) in which the imine double bonds are contained at the bridgehead position in a bicyclo-[3.2.1]octene framework. Although the typical product of reaction of an acyclic α,β-unsaturated ketone with hydrazine is an isoxazoline, such reaction with (1) seemed improbable in view of the high strain energy [6] in bridgehead bicyclo[3.2.1]-octenes, which leads to high reactivity. Experimental support for our structural assignment is found in the chemistry of the bishydrazone (3). Although (3) is unstable in air, darkening rapidly, in the absence of air it is stable at room temperature. Further, acetylation of compound (3) gives the crystalline tetracyclic compound (6), which is not only air stable but also stable at room temperature for many months. Such behaviour is not characteristic of a bridgehead bicyclo[3.2.1]octene. The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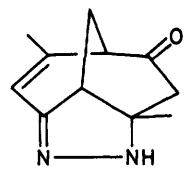
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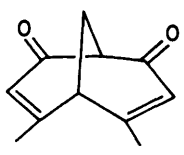
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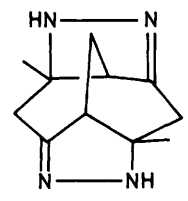
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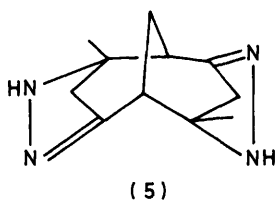
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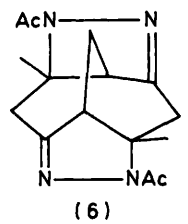
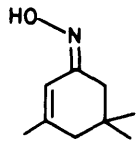

(6)

observed $\nu_{max.}$ 1 615 cm^{-1} (C=N) in (3) is intermediate between the values found for typical imines (1 640—1 690 cm^{-1}) and the exceptionally low value (1600 cm^{-1}) found [7] for a highly strained 2-azabicyclo[3.2.1]non-1-ene. Modest strain in the bishydrazone (3) is indicated. Cleavage reactions of (3) leading to relief of this strain are reported in the following paper.[5] However, little evidence of strain can be found by analysis of the ^{1}H and ^{13}C n.m.r. spectra of (3) and the related amide (6). In particular, the resonance associated with the imine carbon at 160.19 p.p.m. in (3) and at 158.61 p.p.m. in (6) accords with the expected value [8] for unstrained hydrazones.

In contrast to the behaviour of hydrazine, reaction of the dione (1) with 2,4-dinitrophenylhydrazine, or with semicarbazide hydrochloride, gave only hydrazone or semicarbazone products [see Experimental section for the preparation of the hydrazones (17) and (18) and the semicarbazone (19)] which had not undergone the possible additions to lead to products analogous to (2) and (3). Similarly, reaction with hydroxylamine gave oximes of (1) without further cyclisation [see Experimental section for the preparation of the oximes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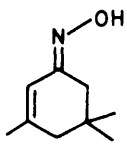
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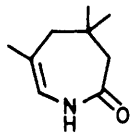
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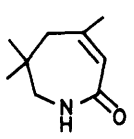
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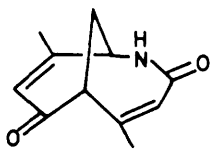
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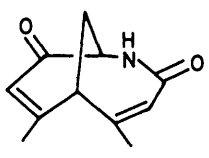
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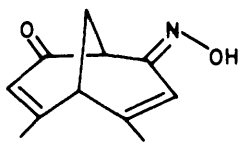
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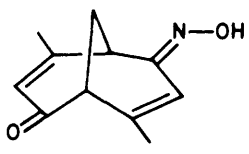
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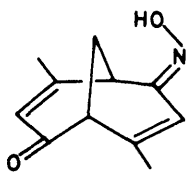
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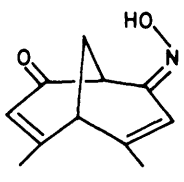
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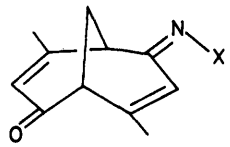
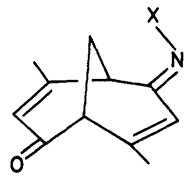
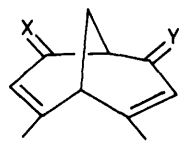
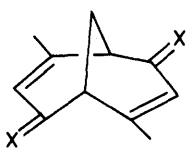

(17) X = NH·$C_6H_3(NO_2)_2$
(22) X = OTs


(18) X = $NHC_6H_3(NO_2)_2$


(21) X = Y = NOH
(23) X = O; Y = NOTs


(19) X = $NNHCONH_2$
(20) X = NOH

(20) and (21)]. In the formation of products from hydrazines or hydroxylamine, complex mixtures might be expected, not only by mono and bis condensation but also by formation of the different possible geometrical isomers. The assignment of structures is facilitated by earlier studies. In particular, the structures of the isomeric isophorone oximes [9,10] have been assigned. In the oxime (7) the resonance associated with the vinyl proton is observed 0.65 p.p.m. downfield relative to the equivalent resonance for oxime (8). Similar shifts are observed [10] in oximes of testosterones. This relative deshielding found in *syn*-oximes is similarly found in *syn*-hydrazones.[11]

Reaction of compound (1) with 2,4-dinitrophenylhydrazine gave two crystalline monohydrazones, which were separated by preparative t.l.c. The structures were assigned on the basis of the relative positions of the resonances associated with the *syn*/*anti* vinyl protons. Reaction of (1) with semicarbazide hydrochloride gave a mixture of bis-semicarbazones which were not separated, while reaction with hydroxylamine hydrochloride again gave either a mixture of the crystalline mono-oximes or a mixture of the crystalline di-oximes with excess of reagent. In the mixture of the mono-oximes the respective *syn*- and *anti*-isomers were recognised by their respective resonances at τ 3.63 and 4.17 [comparative values, τ 3.70 for (7) and τ 4.35 for (8)]. The reactions with 2,4-dinitrophenylhydrazine, semicarbazide hydrochloride, and hydroxylamine differ significantly from the behaviour observed with hydrazine. The absence of further cyclisation can be attributed to the poor nucleophilicity of the heteroatom centres capable of a potential addition. Support for this view is found in the reaction of methylhydrazine, which in giving complex product mixtures appears to give some tricyclic or tetracyclic products. Unfortunately, stable products could not be isolated from this reaction. Reaction with hydrazine is unique in giving a tetracyclic adduct quantitatively.

Cyclisation to give tri- and tetra-cyclic products can occur either from an *endo* direction to give compound (3) as the final product by successive *endo* attacks, or possibly by *exo* attack. Models show that such an *exo* attack is most improbable, and subsequent chemistry [12] dictates that the attack to give (3) is from the *endo* face. Cyclisation probably occurs following hydrazone formation.

Following our formation of the oxime products of the diketone (1) we noted with interest the reported [13] Beckmann rearrangement of a series of oximes including that of the isophorane oximes (7) and (8) to give the two lactams (9) and (10). Similar rearrangement of the oximes of (1) might lead to new bridged nitrogen heterocyclic systems. We, therefore, examined the Beckmann rearrangement of the oximes of (1) and the related compound (4).

Reaction of the dioximes of (1) and (4) under a variety of conditions, and reaction of the mono-oximes of (1) and (4) with either polyphosphoric acid or phosphorus pentaoxide, failed. In most cases only polymeric products were obtained. Using the conditions of Fleming and Woodward [14] requiring prior formation of the *O*-tosyloximes and rearrangement in hydrochloric acid–acetic acid, low yields of lactam products were isolated. However, better yields were obtained by rearrangement of the *O*-tosyloximes (22) and (23) over alumina. From the mixture of isomeric mono-oximes from (1), a single crystalline lactam (11) was isolated in 39% yield following chromatography. Similarly, rearrangement of the mixture of isomeric mono-oximes from (4) gave a single crystalline lactam (12) in 47% yield.

Structures can be assigned to the lactams (11) and (12) by consideration of the ^1H n.m.r. spectra. The relative downfield shifts in (11) of a bridgehead proton which resonates at τ 6.18, and in (12) of a similar bridgehead proton at τ 6.21, establish that the migrating centre in the Beckmann rearrangement is the sp^3 carbon rather than the possible sp^2 centre. Other spectroscopic features are in good agreement with data reported [13] for related oximes.

The observed migratory aptitude may be explained by the preference for formation of derivatives of the *syn*-oximes (13)

and (14) rather than the *anti*-oximes (15) and (16), which are more sterically hindered. However, it should be noted that with related cyclohex-2-enones [10,13] there is again a preference for migration of the sp^3 carbon centre. Hence from the mono-oximes access to 2-azabicyclo[4.3.1]decadienediones is possible, albeit in modest yields. However, we have been unable to induce the double Beckmann rearrangement of the di-oximes to give diazabicyclo[4.4.1]undecadienediones.

Experimental

I.r. spectra were measured for chloroform solutions with a Unicam SP200 spectrophotometer. N.m.r. spectra were measured for deuteriochloroform solutions with a Varian XL-100 instrument with tetramethylsilane as internal standard. U.v. spectra were measured for solutions in ethanol with a Unicam SP800 spectrophotometer. Mass spectra were measured with a Kratos MS30 spectrometer. Column chromatography was carried out on Grace Kieselgel (100-200 mesh). Thin layer chromatography (t.l.c.) was carried out on Merck Kieselgel $60HF_{254+366}$. For analytical work plates of 0.5 mm thickness were used and for preparative separations 1 mm thickness was used. M.p.s were determined for samples in sealed capillary tubes and are uncorrected. Light petroleum refers, unless otherwise stated, to that fraction having b.p. 40—60 °C. Organic solutions were dried over $MgSO_4$.

4,9-Dimethyl-2,3,7,8-tetra-azatetracyclo[7.3.1.0.^{4,12}0^{6,10}]-*trideca-1,6-diene* (3).—4,8-Dimethylbicyclo[3.3.1]nona-3,7-dione [15] (1) (2.0 g) and hydrazine hydrate (1.14 ml) were stirred in ethyl alcohol at room temperature under N_2 for 5 h. Removal of solvent under reduced pressure afforded an off-white solid residue which rapidly turned brown on exposure to air. Recrystallisation from ethyl acetate–diethyl ether (1 : 1) afforded as white crystals 4,9-dimethyl-2,3,7,8-tetra-azatetracyclo[7.3.1.0.^{4,12}0^{6,10}]trideca-1,6-diene (3) (2.4 g), m.p. 155—158 °C; $\nu_{max.}$ ($CHCl_3$) 3 300 and 1 615 cm^{-1}; $\lambda_{max.}$ 268 nm (ε 3 700); M^+ 204; τ($CDCl_3$) 4.58 (2 H, br s, NH), 7.11 (2 H, t, *J* 3 Hz, 10- and 12-H), 7.59 (4 H, s, 5- and 13-H), 8.07 (2 H, t, *J* 3 Hz, 11-H), and 8.50 (6 H, s, 2 × Me); ^{13}C n.m.r. 16.74 (C-11), 24.6 (Me), 39.27 (C-5 and -13), 50.14 (C-10 and -12), 76.18 (C-4 and -9), and 160.19 p.p.m. (C-1 and -6).

The dihydrazone (3) was further characterised by acetylation (Method A, see ref. 5) to give the *diamide* (6) (73.5%), m.p. 252—253 °C (Found: C, 62.1; H, 7.0; N, 19.3. $C_{15}H_{20}N_4O_2$ requires C, 62.48; H, 6.99; N, 19.43%). $\nu_{max.}$ (Nujol) 1 665 and 1 620 cm^{-1}; M^+, 288; τ($CDCl_3$) 7.06 (2 H, t, *J* 3 Hz, 10- and 12-H), 6.90 and 7.74 (4 H, ABq, *J* 14 Hz, 5- and 13-H), 7.74 (6 H, s, COMe), 8.06 (2 H, t, *J* 3 Hz, 11-H), and 8.10 (6 H, s, Me); ^{13}C n.m.r. 16.68 (C-11), 23.59 and 24.53 (Me and COMe), 33.36 (C-5 and -13), 52.43 (C-10 and -12), 75.05 (C-4 and -9), 158.61 (C-1 and -6), and 171.62 p.p.m. (−CO−).

Mono-2,4-dinitrophenylhydrazone of 4,8-Dimethylbicyclo-[3.3.1]*nona-3,7-diene-2,6-dione* (1).—Excess of freshly prepared 2,4-dinitrophenylhydrazine in methanol was added to 4,8-dimethylbicyclo[3.3.1]nona-3,7-diene-2,6-dione (1) (325 mg) in methanol (5 ml) containing conc. sulphuric acid (2 drops). After 2 h at room temperature the precipitate (276 mg) was collected and chromatographed (t.l.c.) with diethyl ether as eluant to give the more polar *hydrazone* (17), m.p. 203—206 °C (Found: C, 56.9; H, 4.6; N, 15.7. $C_{17}H_{16}N_4O_5$ requires C, 57.30; H, 4.53; N, 15.72%); $\nu_{max.}$ ($CHCl_3$) 3 330, 1 670, 1 610, 1 590, and 1 350 cm^{-1}; *m/z* 356 (M^+); τ −1.50 (1 H, br s), 0.81 (1 H, s), 1.70 (1 H, d), 2.03 (1 H, d), 3.76 (1 H, s), 4.30 (1 H, s), 6.67 (1 H, t, *J* 3 Hz), 6.88 (1 H, t, *J* 3 Hz), 7.48 (2 H, t, *J* 3 Hz), 7.85 (3 H, s), and 7.89 (3 H, s); and the less polar *hydrazone* (18), m.p. 175—177 °C (Found: C, 57.0; H, 4.4; N, 15.8. $C_{17}H_{16}N_4O_5$ requires C, 57.30; H, 4.53; N, 15.72%); $\nu_{max.}$ ($CHCl_3$) 3 340, 1 670, 1 615, 1 595, 1 345, and 1 325 cm^{-1}; *m/z* 356 (M^+); τ −1.75 (1 H, br), 0.86 (1 H, s), 1.64 (1 H, d), 1.95 (1 H, d), 3.94 (1 H, s), 4.20 (1 H, s), 6.31 (1 H, t, *J* 3 Hz), 6.96 (1 H, t, *J* 3 Hz), 7.52 (2 H, t, *J* 3 Hz), 7.85 (3 H, s), and 8.00 (3 H, s).

Bis-semicarbazone of 4,8-Dimethylbicyclo[3.3.1]*nona-3,7-diene-2,6-dione*.—Semicarbazide hydrochloride (620 mg) in an aqueous phosphate buffer (pH 5.6) was added to 4,8-dimethylbicyclo[3.3.1]nona-3,7-diene-2,6-dione (1) (444 mg) in ethanol (20 ml). The solution was stirred at room temperature for 20 h and then cooled to 0 °C. Filtration afforded a solid residue which was washed with water (10 ml) and dried to give as a mixture of isomers the bis-semicarbazone (19) of 4,8-dimethylbicyclo[3.3.1]nona-3,7-diene-2,6-dione (451 mg, 62%), m.p. 290 °C (decomp.), $\nu_{max.}$ 3 410, 3 180, 1 680, and 1 590 cm^{-1}; τ[$(CD_3)_2SO$] 0.25 (2 H, s, NH), 3.55 (2 H, m, 3- and 7-H), 3.73 (4 H, s, NH_2), 5.67 [1 H, m, 1- and 5-H, (*Z*)-isomer], 7.10 [1 H, m, 1- and 5-H, (*E*)-isomer], 8.00 (2 H, m, 9-H), and 8.12 (6 H, m, 4- and 8-Me) (Found: *M*, 290.1534. Calc. for $C_{13}H_{18}N_6O_2$: *M*, 290.1491).

4,8-Dimethylbicyclo[3.3.1]*nona-3,7-diene-2,6-dione 2-Oximes* (13) *and* (15).—4,8-Dimethylbicyclo[3.3.1]nona-3,7-diene-2,6-dione (1) (1.4 g) was dissolved in ethanol (50 ml) and hydroxylamine hydrochloride (0.76 g) in an aqueous phosphate buffer (pH 5.6) was added. The solution was left at room temperature for 3 days, the solvent was removed under reduced pressure, and the residue was partitioned between water (50 ml) and diethyl ether (3 × 50 ml). The combined organic layers were washed with water (2 × 50 ml) and dried ($CaCl_2$). Filtration and removal of the solvent under reduced pressure afforded the *4,8-dimethylbicyclo*[3.3.1]*nona-3,7-diene-2,6-dione 2-oximes* (13) and (15) (1.06 g; 82%) as a mixture of isomers, m.p. 169—172 °C (Found: C, 69.2; H, 6.9. $C_{11}H_{13}NO_2$ requires C, 69.09; H, 6.85%); $\nu_{max.}$ (Nujol) 3 250, 1 660, and 1 635 cm^{-1}; M^+ 191. The ^{1}H n.m.r. spectrum showed a mixture of isomers.

4,6-Dimethylbicyclo[3.3.1]*nona-3,6-diene-2,8-dione 2-Oximes* (14) *and* (16).—4,6-Dimethylbicyclo[3.3.1]nona-3,6-diene-2,8-dione [15] (4) (2.2 g) was dissolved in ethanol (100 ml) and hydroxylamine hydrochloride (1.52 g) in an aqueous phosphate buffer (pH 5.6) was added. The solution was left at room temperature for 3 days, the solvent was removed under reduced pressure, and the residue was partitioned between water (50 ml) and diethyl ether (3 × 50 ml). The combined organic layers were washed with water (2 × 50 ml) and dried ($CaCl_2$). Filtration and removal of the solvent under reduced pressure afforded 4,6-dimethylbicyclo[3.3.1]nona-3,6-diene-2,8-dione 2-oximes (14) and (16) (1.48 g; 62%) as a mixture of isomers, $\nu_{max.}$ 3 250, 1 660, and 1 640 cm^{-1}, *m/z* 191 (M^+). The ^{1}H n.m.r. spectrum showed a mixture of isomers.

4,8-Dimethylbicyclo[3.3.1]*nona-3,7-diene-2,6-dione Dioxime* (20).—4,8-Dimethylbicyclo[3.3.1]nona-3,7-diene-2,6-dione (1) (2.03 g) was dissolved in ethanol (50 ml) and hydroxylamine hydrochloride (2.51 g) in aqueous phosphate buffer (pH 5.6) was added. The solution was heated under gentle reflux for 16 h, the solvent was removed under reduced pressure, and the residue was partitioned between water (50 ml) and diethyl ether (3 × 75 ml). The combined organic layers were dried ($CaCl_2$). Filtration and removal of the solvent under reduced pressure afforded *4,8-dimethylbicyclo*[3.3.1]-*nona-3,7-diene-2,6-dione dioxime* (20) (2.01 g, 83%) as a mix-

ture of isomers, m.p. 181—183 °C (Found: C, 63.9; H, 6.8. $C_{11}H_{14}N_2O_2$ requires C, 64.06; H, 6.84%); $\nu_{max.}$ 3 250 and 1 635 cm^{-1}; M^+ 206. The ^1H n.m.r. spectrum showed a mixture of isomers.

4,6-*Dimethylbicyclo*[3.3.1]*nona*-3,6-*diene*-2,8-*dione Dioxime* (21).—4,6-Dimethylbicyclo[3.3.1]nona-3,6-diene-2,8-dione (4) (1.16 g) was dissolved in ethanol (60 ml) and hydroxylamine hydrochloride (1.38 g) in an aqueous phosphate buffer (pH 5.6) was added. The solution was heated under reflux for 18 h, the solvent was removed under reduced pressure, and the residue was partitioned between water (50 ml) and diethyl ether (3 × 50 ml). The combined organic layers were dried ($CaCl_2$). Filtration and removal of the solvent under reduced pressure afforded 4,6-*dimethylbicyclo*-[3.3.1]*nona*-3,6-*diene*-2,8-*dione dioxime* (21) (0.99 g, 79%) as a mixture of isomers, m.p. 198—200 °C (Found: C, 63.9; H, 6.7. $C_{11}H_{14}N_2O_2$ requires C, 64.06; H, 6.84%); $\nu_{max.}$ (Nujol) 3 250 and 1 635 cm^{-1}; M^+ 206. The ^1H n.m.r. spectrum showed a mixture of isomers.

5,9-*Dimethyl*-2-*azabicyclo*[4.3.1]*deca*-4,8-*diene*-3,7-*dione* (11).—4,8-Dimethylbicyclo[3.3.1]nona-3,7-diene-2,6-dione 2-oxime (13) and (15) (1.01 g) was dissolved in dry pyridine (15 ml) and cooled to 0 °C. Following the addition of toluene-*p*-sulphonyl chloride (1.58 g) the solution was kept at room temperature for 30 min, and then poured into water (100 ml). Extraction with diethyl ether (2 × 50 ml) afforded an extract which was washed with 10% hydrochloric acid (2 × 50 ml) and then with water (2 × 50 ml). The ethereal solution was dried, filtered, and the solvent removed to give 4,8-dimethylbicyclo[3.3.1]nona-3,7-diene-2,6-dione 2-(*O*-tosyloxime) (22) (1.65 g, 90%).

The toluene-*p*-sulphonate (22) was dissolved in the minimum amount of benzene and adsorbed from benzene onto a column of alumina (70 g; Brockmann Grade I). After 18 h the column was eluted with benzene to afford 4,8-dimethylbicyclo-[3.3.1]nona-3,7-diene-2,6-dione 2-(*Z*)-(*O*-tosyloxime) (22) (528 mg, 32%). Further elution with chloroform–methanol (19 : 1) afforded 5,9-dimethyl-2-azabicyclo[4.3.1]deca-4,8-diene-3,7-dione (11) contaminated with a trace of toluene-*p*-sulphonic acid. Recrystallisation from ethyl acetate afforded the pure *lactam* (11) (356 mg, 39%), m.p. 177 °C (decomp.) (Found: C, 68.9; H, 6.8. $C_{11}H_{13}NO_2$ requires C, 69.09; H, 6.85%); *m/z* 191 (M^+), $\nu_{max.}$ ($CHCl_3$) 3 200, 1 670, 1 650, and 1 610 cm^{-1}, $\lambda_{max.}$ 225 (ε 10 100) and 332 nm (ε 79); τ 1.34 (1 H, br d, *J* 6 Hz, NH), 4.03 (1 H, br s, 4-H), 4.14 (1 H, br s, 8-H), 6.18 (1 H, t, *J* 6 Hz, 1 H), 6.75 (1 H, dd, *J* 2 and 4 Hz, 6-H), 7.40 (1 H, ddd, *J* 2, 4, and 14 Hz, 10a-H), 7.71 (1 H, ddd, *J* 2, 2, and 14 Hz, 10b-H), 7.95 (3 H, s, 9-Me), and 7.99 (3 H, s, 5-Me).

5,7-*Dimethyl*-2-*azabicyclo*[4.3.1]*deca*-4,7-*diene*-3,9-*dione* (12).—4,6-Dimethylbicyclo[3.3.1]nona-3,6-diene-2,8-dione 2-oxime (14) and (16) (256 mg) was dissolved in dry pyridine (7 ml) and cooled to 0 °C. Following the addition of toluene-*p*-sulphonyl chloride (371 mg) the solution was kept at room temperature for 1 h and then poured into water (50 ml). Extraction with diethyl ether (2 × 50 ml) afforded an organic extract which was washed with 10% hydrochloric acid (2 × 50 ml) and then with water (2 × 50 ml). The ethereal solution was dried, filtered, and the solvent removed to give 4,6-dimethylbicyclo[3.3.1]nona-3,6-diene-2,8-dione 2-(*O*-tosyloxime) (23) (321 mg, 69%).

The toluene-*p*-sulphonate (23) was dissolved in benzene and adsorbed onto a column of alumina (5 g; Brockmann Grade I). After 18 h the column was eluted with chloroform to afford 4,6-dimethylbicyclo[3.3.1]nona-3,6-diene-2,8-dione 2-(*Z*)-(*O*-tosyloxime) (23) (143 mg, 44%). Further elution with methanol afforded 5,7-dimethyl-2-azabicyclo[4.3.1]deca-4,7-diene-3,8-dione (84 mg, 47%). Recrystallisation afforded the *dione* (12) (ethyl acetate), m.p. 216 °C (decomp.) (Found: C, 68.8; H, 7.0. $C_{11}H_{13}NO_2$ requires C, 69.09; H, 6.85%), *m/z* 191 (M^+) and 163 ($M^+ - CO$); $\nu_{max.}$ ($CHCl_3$) 3 350, 1 670, and 1 610 cm^{-1}. $\lambda_{max.}$ 220 (ε 14 080), 232 (12 180), 335 (170), and 350 nm (150); τ 3.42 (1 H, br, NH), 4.05 (2 H, m, 4- and 8-H), 6.21 (1 H, br m, 1-H), 6.90 (1 H, d, *J* 6 Hz, 6-H), 7.44 (1 H, dt, *J* 6 and 15 Hz, 10a-H), 7.66 (1 H, dt, *J* 2 and 15 Hz, 10b-H), 7.81 (3 H, s, 7-Me), and 7.86 (3 H, s, 5-Me).

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