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CYCLOPENTAANNULATION REACTIONS BETWEEN NITROCYCLOALKENES AND DIACETYL MORPHOLINO ENAMINE

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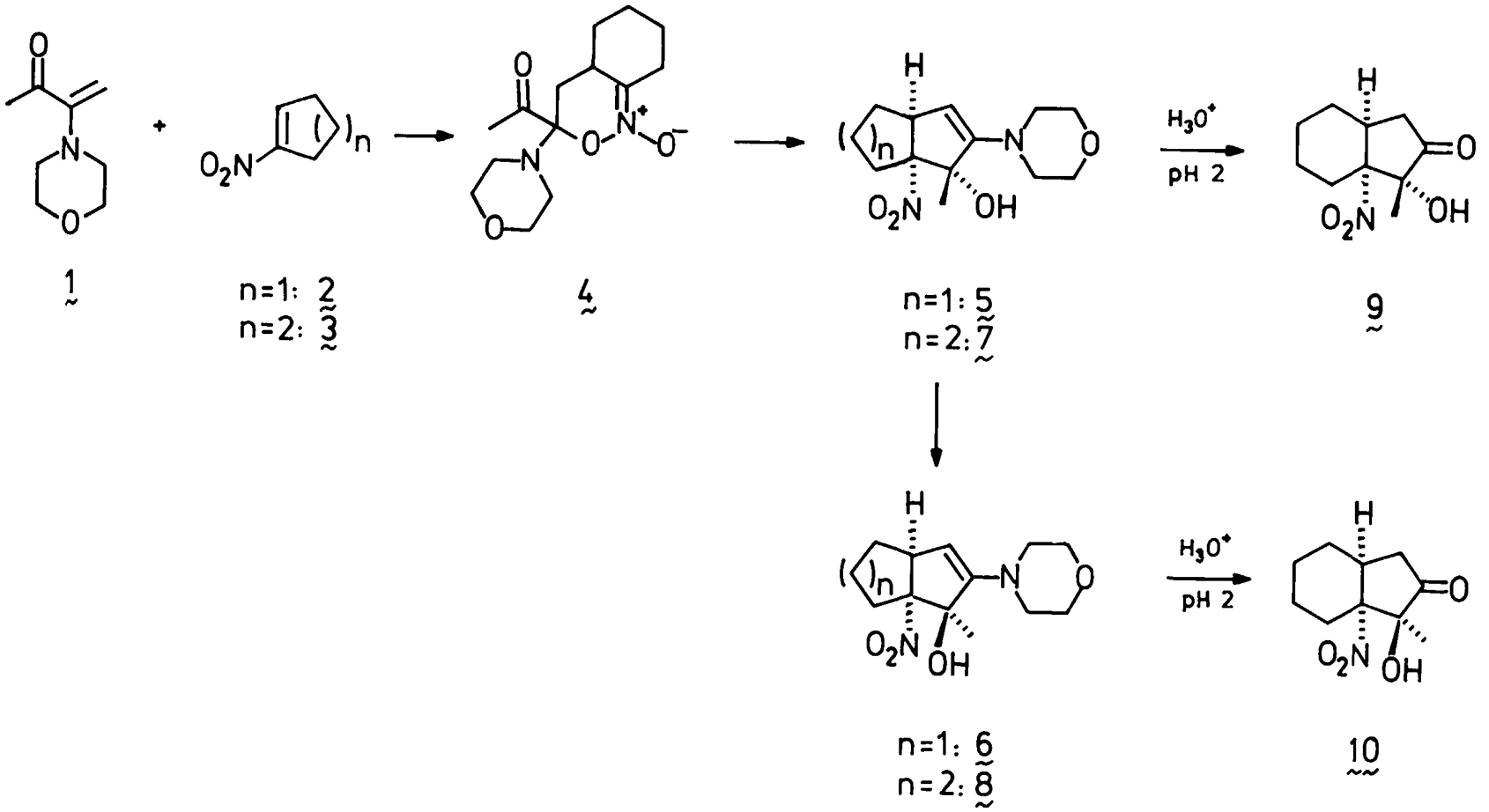
Abstract - Hexahydro-pentalene and -indene nitroalcohols are obtained by reaction of 3-(4-morpholinyl)-3-buten-2-one with cyclic nitroolefins. With 1-nitro-cyclohexene a [4 + 2] heterocyclization intermediate is separated, while an unusual product of double addition is obtained from the hexahydro-pentalene derivative in aqueous acidic medium.

Nitroolefins are known to react as 4π electron donors with enamines to give products of [4 + 2] heterocycloaddition more frequently[1,2] and as 2π electron donors to give products of [2 + 2] cycloaddition more rarely.[3,4] [3 + 3] Carbocyclization reactions of enamines with suitably substituted nitroolefins are also known.[5] We report here a polar [3 + 2] cyclization reaction[6] between two nitrocycloalkenes and a particular enamine substrate, namely the α-ketoenamine derived from diacetyl and morpholine.[7]

The α-ketoenamine 1 is reacted with 1-nitrocyclopentene (2) and 1-nitro-cyclohexene (3) (Scheme 1). In this latter reaction, which we will examine first, the product of kinetic control is the 1,2-oxazine N-oxide system 4 which probably derives from a two-step[8,9] [4 + 2] heterocyclization reaction. This compound is formed in 95% yield by simple mixing the reagents at low temperature (-5°C ~ 0°C) in the absence of solvent, as it is usual for the α-ketoenamines.[10] The 1,2-oxazine N-oxide system thus obtained, whose stereochemistry is not assigned, is surprisingly stable in solid state and can be stored for months at room temperature. When however it is dissolved in a solvent, it undergoes nucleophilic ring fission to the dipolar intermediate 11, followed by recyclization to give the corresponding hexahydroindene derivative 7 through the betaine type system 12.

Scheme 1


O
N
O
1
+
O_2N
)n
n=1: 2
n=2: 3
O
N
O
N+
O−
4
H
)n
O_2N
OH
N
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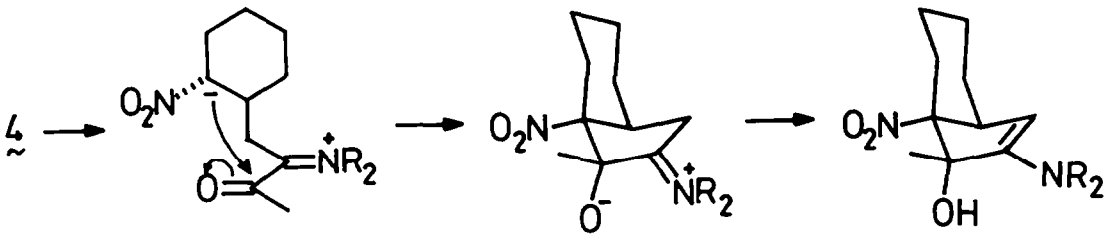
n=1: 5
n=2: 7
H_3O^+
pH 2
O
9
n=1: 6
n=2: 8
10



11 12 7

The compound 7, which is enamine in nature, is in turn a product of kinetic formation, as it isomerizes into its diastereoisomer 8 when left in a protic solvent for several hours. The instability of the enamine 7 is probably due to the steric interaction between the methyl group and the morpholine ring which prevents the base from rotating freely. This steric inhibition to rotation is clearly evident in the proton 300 MHz ^1H NMR spectrum of compound 7, in which the methylene groups adjacent to the nitrogen atom are split into two resonances (3.05 and 2.65 ppm). This splitting is in fact no longer present in the spectrum of the diastereoisomer 8, in which the above mentioned interaction is relieved. This situation is also reflected in the conjugating power of the morpholine nitrogen with the double bond, expressed by the chemical shifts of the corresponding vinyl protons (4.65 ppm in 7 and 4.25 ppm in 8). The isomerization of the system 7 into 8 might be considered a simple retro-Henry reaction, in which only the two adjacent chiral centres C-1 and C-7a are involved. This interpretation however is an oversimplification as it will appear later on when the behaviour of the corresponding diastereoisomeric ketones is considered.

Hydrolysis of the enamine derivative 7, carried out at pH 5, is very slow, and the equilibration into the diastereoisomer 8 takes place preferentially, giving eventually the corresponding ketone 10. At pH 2 hydrolysis is fast enough to leave the chiral centres of compound 7 unchanged, leading to the isolation of the corresponding ketone 9. The ketone 10 has been analysed by X-ray and this determination allowed all the structural assignments to be made. The molecular structure of the ketone 10 together with the atomic labelling scheme are shown in Fig. 1. Crystals of 10 consist of monomeric $C_{10}H_{15}NO_4$ units, linked by close intermolecular hydrogen bonds. The O1-O4' distance (2.846 Å) in fact suggests the existence of an intermolecular hydrogen bond between the hydrogen atom of the hydroxy group and the carbonyl carbon atom of another molecule, as shown also by the presence of a peak in the difference map attributable to the hydrogen atom of the bent O1-H..O4' bridge.

The crystallographic results clearly show that the fusion between the rings is cis, the nitro group occupying an axial position with respect to the six-membered ring. This latter cycle is flattened along the junction as indicated by the values

of the relative torsional angles (C5-C4-C3a-C7a, 45.7°; C4-C3a-C7a-C7, -45.4°; C3a-C7a-C7-C6, 54.6°). No intramolecular hydrogen bonding between the nitro group and the adjacent hydroxy group is observed.

TABLE 1 - Crystal Data

Formula	$C_{10}H_{15}NO_4$
molecular weight	213.2
crystal class	orthorombi
Z	4
space group	$P2_12_12_1$
a, Å	7.238(1)
b, Å	10.269(1)
c, Å	14.333(3)
ρ_{calc}	1.329
V, Å^3	1065.3
$\lambda(MoK_\alpha)$, Å	0.7107
$\mu(MoK_\alpha)$, cm^{-1}	0.96
unique data	1365
unique data with I>3σ(I)	741
R	0.069
R_w	0.103

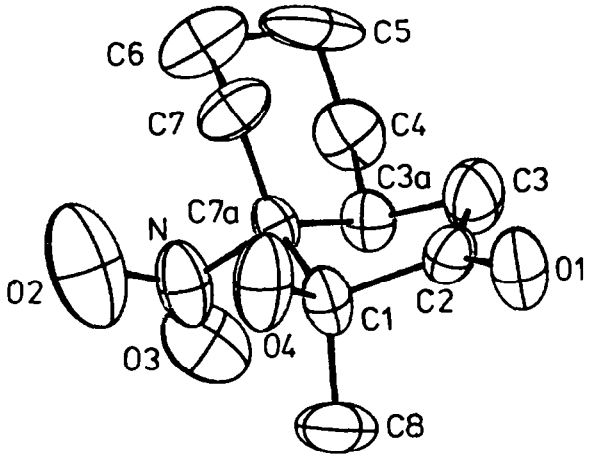


FIG. 1 - ORTEP drawing of the ketone 10 with labelling scheme. Hydrogen atoms are omitted.

TABLE 2 - Positional Parameters and Their Estimated Standard Deviations

Atom	x	y	z	B(Å^2)
O1	0.0441(8)	0.2248(5)	0.4920(4)	5.2(1)
O2	-0.232(1)	-0.2096(7)	0.3144(7)	10.21(3)
O3	-0.050(1)	-0.2788(6)	0.4201(6)	7.8(2)
O4	-0.2467(8)	0.0968(5)	0.3988(4)	5.3(1)
N	-0.104(1)	-0.1941(7)	0.3671(6)	5.6(2)
C1	-0.092(1)	0.0292(7)	0.4380(5)	3.5(2)
C2	0.062(1)	0.1197(7)	0.4579(5)	3.4(2)
C3	0.239(1)	0.056(1)	0.4305(6)	5.7(2)
C3a	0.187(1)	-0.0819(8)	0.3996(6)	3.8(2)
C4	0.321(1)	-0.144(1)	0.3262(7)	5.9(2)
C5	0.302(2)	-0.0820(9)	0.2311(7)	9.9(3)
C6	0.091(2)	-0.082(1)	0.1992(7)	7.4(3)
C7	-0.018(1)	-0.0063(8)	0.2679(5)	4.7(2)
C7a	-0.0074(9)	-0.0637(7)	0.3641(5)	3.0(1)
C8	-0.140(1)	-0.037(1)	0.5313(7)	6.1(2)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3*[a^2*B(1,1)+b^2*B(2,2)+c^2*B(3,3)+ab(\cos\gamma)*B(1,2)+ac(\cos\beta)*B(1,3)+bc(\cos\alpha)*B(2,3)]$

Since in the products of thermodynamic control 8 and 10 the fusion between the rings is cis, it is likely that also in the compound of kinetic control 7 and 9 it is also cis. This is supported by the 300 MHz ^{1}H NMR spectra of the octahydroindanone derivatives 9 and 10 (Fig. 2), in which, apart from a few resonances which move upfield or downfield as a consequence of a change in chirality of C-1, the skeleton absorptions are practically superimposable.

Quite surprisingly, the ketone 9 cannot be isomerized into its diastereoisomer 10 under acidic and basic conditions, which must be however mild to avoid undesired by-products. This is in strong contrast with the behaviour of the enamines

from which they derive and it suggests that the amine component could participate in the equilibration reaction.

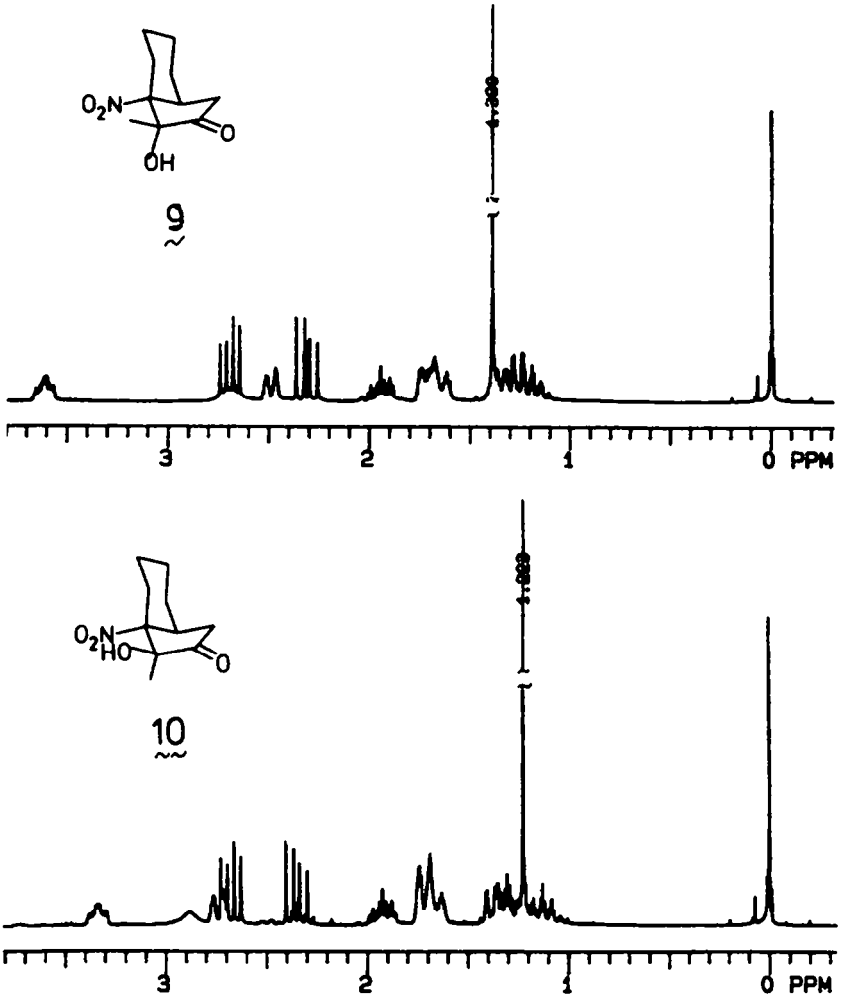


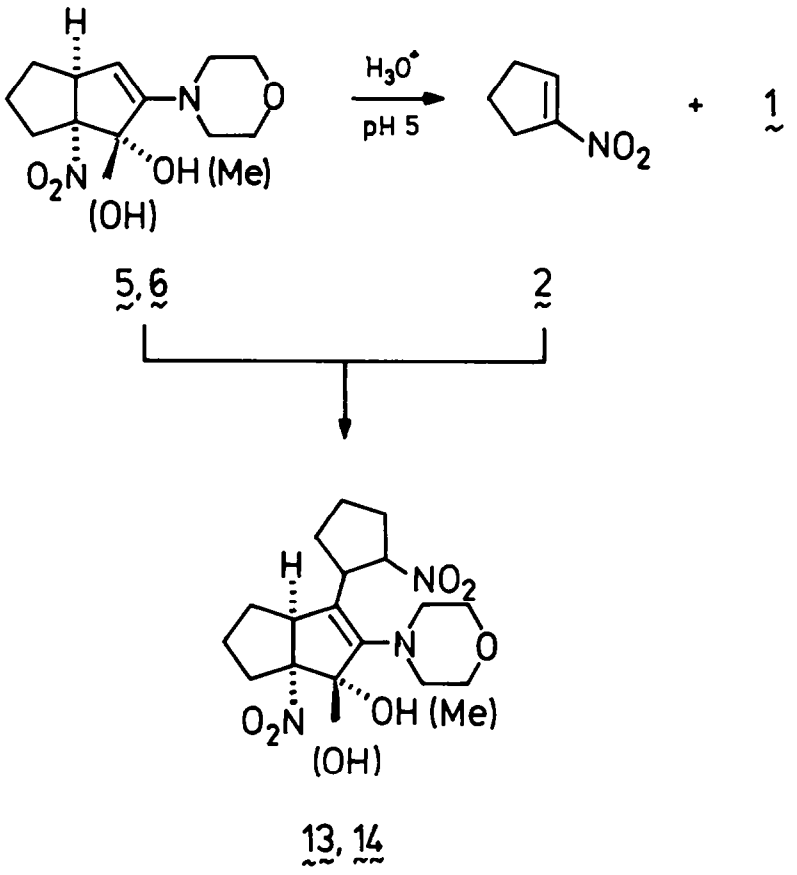
FIG. 2 - 300 MHz ^{1}NMR spectra of the ketones 9 and 10.

The reaction of the α-ketoenamine 1 with 1-nitrocyclopentene (3) is quite similar, except for the fact that the corresponding 1,2-oxazine N-oxide derivative, whose formation and rapid trasformation can be seen by IR spectroscopy, could not be isolated. Again the compound of kinetic control is an enamine, namely the hexahydro-pentalene derivative 5, which isomerizes into its diastereoisomer 6, just as its homolog 7.

The spectroscopic data of both the enamines 5 and 6 are very similar to those of 7 and 8, thus indicating that their stereochemistry is the same. On the contrary, any attempt to hydrolyse compounds 5 and 6 to the corresponding pentalenone derivatives failed, under the most varied conditions of pH and solvent. Interestingly at pH 4-5 two diastereoisomeric nitroalkylated enamines 13 and 14 are formed, the former from compound 5, the latter from compound 6. These systems are

formed by partial reversion of each hexahydropentalene derivative to the reactants, catalysed by acidic conditions. While 1-nitrocyclopentene is formed, it reacts immediately with the remainder of the hexahydropentalene derivative, as indicated in Scheme 2. The corresponding Michael-type addition products 13 or 14 are formed as shown also by performing the reactions between the enamines 5 and 6 and the nitroolefin 2.

Scheme 2



This result is most surprising because, as far as we know, it is the first case in the enamine chemistry[11] in which, in acidic aqueous medium, a trisubstituted cycloalkanone enamine, instead of undergoing hydrolysis, reacts further as a Michael-type donor system.

EXPERIMENTAL

Melting points were determined with a Büchi apparatus and are uncorrected. IR spectra were recorded in nujol mulls on a Perkin-Elmer 1320 spectrometer. ^1H NMR spectra were measured on Varian 360 A (60 MHz) and Varian VXR (300 MHz) spectrometers using deuterochloroform as solvent and tetramethylsilane as internal standard. ^{13}C NMR spectra were recorded on Bruker WP-80 (20.1 MHz). MS spectra were obtained on a VG 7070 spectrometer at 70 eV. TLC were performed on Whatman K6F silica gel plates.

Reaction of 3-(4-morpholinyl)-3-buten-2-one (1) with 1-nitrocyclopentene (2)

The nitroolefin 2 (0.6 g, 5.2 mmol) is added to the α-ketoenamine 1 (0.8 g, 5.2 mmol) at -20 °C. After 24 h at -18 °C, the solid is filtered (1.3 g, 95%) with the aid of a small amount of ether. The product is identified as [3aR*-(3aα,4α,6aα)]-

4-hydroxy-4-methyl-5-(4-morpholinyl)-3a-nitro-1,2,3,3a,4,6a-hexahydro-pentalene (5), m.p. 143-145 °C (Found: C, 58.23; H, 7.46; N, 10.38%); IR, ν_{max}, cm^{-1}: 3360 (OH), 1615 (C=C), 1520 (NO_2), 1100 (C-O-C); ^1H NMR, δ; 4.7 (d, J 2.0 Hz, 1 H, C=CH), 4.1 (bd, 1 H, H-6a), 3.8 (m, 4 H, CH_2OCH_2), 3.4-1.3 (m + s, 14 H), 1.6 ppm (s, Me); ^{13}C NMR, δ: 150.8 (s), 109.6 (d), 108.4 (s), 82.3 (s), 66.5 (2 t), 50.4 (2 t), 47.3 (d), 36.2 (t), 30.6 (t), 24.9 (t), 20.5 (q).MS: M^+ 268 (1), 222 (3), 221 (3), 135 (2), 111 (76), 43 (100).

In chloroform solution the enamine 5 isomerizes into the corresponding derivative 6, identified as [3aR*-(3aα,4β,6aα)]-4-hydroxy-4-methyl-5-(4-morpholinyl)-3a-nitro-1,2,3,3a,4,6a-hexahydro-pentalene, m.p. 164-166 °C (Found: C, 58.35; H, 7.55; N, 10.38. $C_{12}H_{20}N_2O_4$ requires: C, 58.19; H, 7.51; N, 10.44%); IR, ν_{max}, cm^{-1} 3380 (OH), 1620 (C=C), 1525 (NO_2), 1110 (C-O-C); ^1H NMR, δ: 4.3 (d, J 2.0 Hz, C=CH), 3.8 (m, 5 H, CH_2OCH_2, H-6a), 3.1 (m, 4 H, CH_2NCH_2), 2.7 (m, 1 H), 2.45-1.50 (m, 7 H), 1.4 (s, 3 H, Me), 1.2 (m, 1 H); ^{13}C NMR, δ: 149.6 (s), 111.9 (s), 102.1 (d), 82.8 (s), 66.8 (2 t), 49.0 (2 t), 46.5 (d), 35.3 (t), 31.5 (t), 25.1 (q), 24.6 ppm (t). MS: M^+ 268 (15), 222 (43), 221 (40), 135 (21), 112 (19), 111 (38), 43 (100).

Reaction of 3-(4-morpholinyl)-3-buten-2-one (1) with 1-nitrocyclohexene (3)

The nitroolefin 3 (0.70 g, 5.5 mmol) is added to the ketoenamine 1 (0.85 g, 5.5 mmol) in an ice bath. The mixture is kept at -18 °C for 15 h. Addition of a small amount of ether to the solidified mass allows the product 4 to be isolated (1.4 g, 90% yield) and identified as 3-acetyl-4,4a,5,6,7,8-hexahydro-3-(4-morpholinyl)-3H-2,1-benzoxazine N-oxide, m.p. 134-135 °C (Found: C, 59.63; H, 7.90; N, 9.85. $C_{14}H_{22}N_2O_4$ requires: C, 59.56; H, 7.85; N, 9.92%); IR, ν_{max}, cm^{-1}: 1725 (C=O), 1610 (C=N), 1115 (C-O-C); ^1H NMR, δ: 3.7 (m, 4 H, CH_2OCH_2), 3.4-2.4 (m, 5 H, CH_2NCH_2, H-4a), 2.3 (s, 3 H, Me), 2.3-1.0 ppm (m, 10 H). MS: M^+ 282 (7), 265 (3), 235 (26), 170 (21), 81 (100).

When the oxazine 4 is dissolved in methanol at room temp., the product 7 precipitates, [1R*-(1α,3aα,7aα)]-3a,4,5,6,7,7a-hexahydro-1-hydroxy-1-methyl-2-(4-morpholinyl)-7a-nitro-1H-indene, m.p. 180-182 °C (Found: C, 59.50; H, 7.78; N, 9.98. $C_{14}H_{22}N_2O_4$ requires: C, 59.56; H, 7.85; N, 9.92%); IR, ν_{max}, cm^{-1}: 3340 (OH), 1625 (C=C), 1530, 1365 (NO_2), 1105 (C-O-C); ^1H NMR (300 MHz), δ: 4.65 (d, J 1.8 Hz, 1 H, C=CH), 3.88 (dd, J_1 1.8 Hz, J_2 3.6 Hz, 1 H, H-3a), 3.75 (m, 4 H, CH_2OCH_2), 3.05 (m, 2 H, CH_2N), 2.65 (m, 2 H, CH_2N), 2.4 (dsept, J_1 14.4 Hz, J_2 1.5 Hz, 1 H), 2.1 (bs, 1 h, OH), 1.9-1.6 (m, 5 H), 1.55 (s, 3 H, Me), 1.15 ppm (m, 2 H). ^{13}C NMR: 149.6 (s), 110.4 (d), 98.6 (s), 84.8 (s), 66.6 (2 t), 50.6 (2 t), 39.9 (d), 30.9 (t), 25.3 (t), 21.8 (t), 20.9 (t), 18.2 ppm (q). MS: M^+ 282 (1), 265 (0.4), 236 (5), 235 (7), 220 (1), 125 (17), 43 (100).

When the system 7 is left in either methanol or chloroform for a few days, it converts into its isomer 8, [1R*-(1α,3aβ,7aβ)]-3a,4,5,6,7,7a-hexahydro-1-hydroxy-1-methyl-2-(4-morpholinyl)-7a-nitro-1H-indene, m.p. 164-165 °C, from methanol (Found: C, 59.63; H, 7.90; N, 9.85. $C_{14}H_{22}N_2O_4$ requires: C, 59.56; H, 7.85; N, 9.92%); IR, ν_{max}, cm^{-1}: 3370 (OH), 1625 (C=C), 1530, 1355 (NO_2), 1110 (C-O-C); ^1H NMR (300 MHz), δ: 4.25 (d, J 1.5 Hz, 1 H, C=CH), 3.75 (t, 4 H, CH_2NCH_2), 2.45 (bs, 1 H, OH), 2.40 (dsept, J_1 14.7 Hz, J_2 1.5 Hz, 1 H), 2.1 (ddd, J_1 14.7 Hz, J_2 13.9 Hz, J_3 3.6 Hz, 1 H), 1.90-1.52 (m, 4 H), 1.33 (s, Me), 1.36-0.96 ppm (m and s, 5 H); ^{13}C NMR: 155.6 (s), 112.0 (s), 101.7 (d), 85.3 (s), 66.8 (2 t), 48.9 (2 t), 39.2 (d), 30.1 (t), 25.5 (q), 21.8 (t), 21.5 (t), 21.1 ppm (t). MS: M^+ 282 (1), 265 (0.5), 252 (0.4), 236 (5), 235 (6), 220 (1), 170 (6), 125 (30), 43 (100).

Hydrolyses of the enamines 7 and 8

The enamine 7 is hydrolysed in methanol-water, at pH 2, at room temp. for 4 h, to give the ketone 9, [1R*-(1α,3aα,7aα)]-1-hydroxy-1-methyl-7a-nitro-octahydro-2H-inden-2-one, m.p. 128-129 °C, from ethylacetate (Found: C, 56.38; H, 7.12; N, 6.50. $C_{10}H_{15}NO_4$ requires: C, 56.33; H, 7.09; N, 6.57%); IR, ν_{max}, cm^{-1}: 3590 (OH), 1760 (C=O), 1545, 1382 (NO_2); ^1H NMR (300 MHz), δ: 3.62 (tddd, J_1 12.1 Hz, J_2 9.2 Hz, J_3 5.1 Hz, J_4 2.5 Hz, 1 H, H-3a), 2.7 (bs, 1 H, OH), 2.49 (bdd, J_1 14.7 Hz, 1 H), 2.71, 2.31 (dq, part AB of an ABX system, J_{AB} 19.6 Hz, J_{AX} 12.1 Hz, J_{BX} 9.2 Hz, 2 H, H-3), 1.95 (tdd, J_1 4.7 Hz, J_2 14.7 Hz, J_3 13.6 Hz, 1 H), 1.7 (m, 3 H), 1.39 (s, 3 H, Me), 1.25 ppm (m, 2 H); ^{13}C NMR, δ: 210.3 (s), 94.2 (s), 80.0 (s), 37.6 (t), 32.4 (d), 28.4 (t), 22.9 (t), 21.0 (t), 18.4 (t), 15.2 ppm (q); MS: 166 (0.6), 165 (0.6), 137 (1), 125 (32), 43 (100).

The enamine 8 is hydrolysed under the same conditions as above, to yield the ketone 10 [1R*-(1α,3aβ,7aβ)]-1-hydroxy-1-methyl-7a-nitro-octahydro-2H-inden-2-one, m.p. 99-100 °C, from ethylacetate (Found: C, 56.45; H, 7.15; N, 6.52. $C_{10}H_{15}NO_4$ requires: C, 56.33; H, 7.09; N, 6.57%); IR, ν_{max}, cm^{-1}: 3570, 3540 (OH), 1755 (C=O), 1540, 1360, 1340 (NO_2); ^1H NMR (300 MHz), δ: 3.32 (tddd, J_1 2.2 Hz, J_2 4.9 Hz, J_3 10.1 Hz, J_4 12.0 Hz, 1 H, H-3a), 2.88 (bs, 1 H, OH), 2.74 (bd, 1 H), 2.68, 2.34 (dq, part AB of an ABX system, J_{AB} 20.0 Hz, J_{AX} 10.1 Hz, J_{BX} 12.0 Hz, 2 H, H-3), 1.93 (tt, J_1 14.1 Hz, J_2 4.7 Hz, 1 H), 2.0 (m, 3 H), 1.4-1.0 (m and s, 6 H), 1.22 ppm (s, Me); ^{13}C NMR, δ: 212.4 (s), 95.4 (s), 82.6 (s), 35.8 (t), 31.4 (d), 27.6 (t), 23.2 (t), 20.6 (t), 19.9 (q), 18.6 ppm (t); MS: 166 (0.2), 165 (0.2), 125 (28), 43 (100).

Reactions of the enamines 5 and 6 with 1-nitrocyclopentene (2)

The nitroolefin 2 (0.08 g, 0.75 mmoles) is added to a solution of the enamine 5 (0.2 g, 0.75 mmoles) in dry ether, at 0 °C. After a few hours a crystalline product is filtered (0.25 g 90% yield), 13, [3aR*-(1R*(or S*),2R*(or S*) 3aα,4α,6aα)]-4-hydroxy-4-methyl-5-(4-morpholinyl)-3a-nitro-6-(2-nitro-cyclo-pentyl)-2,3,3a,4,5-hexahydropentalene, m.p. 136 °C (Found: C, 56.58; H, 7.10; N, 11.10. $C_{18}H_{27}N_3O_6$ requires: C, 56.68; H, 7.13; N, 11.02%); IR, ν_{max}, cm^{-1}: 3340 (OH), 1660 (C=C), 1545, 1530, 1365, 1355 (NO_2), 1100 (C-O-C); ^1H NMR, δ: 5.0 (m, 1 H, $CHNO_2$), 4.0 (m, 1 H, H-6a), 3.7 (m, 5 H, CH_2OCH_2, OH), 3.0 (m, 4 H, CH_2NCH_2), 2.7-1.3 (m and s, 16 H), 1.6 ppm (s, Me); ^{13}C NMR, δ: 148.9 (s), 138.1 (s), 106.9 (s), 89.6 (d), 83.1 (s), 67.4 (2 t), 51.8 (2 t), 49.4 (d), 45.1 (d), 35.8 (t), 32.1 (t), 31.1 (t), 29.8 (t), 24.9 (t), 23.7 (t), 21.6 ppm (q); MS: M^+ 381 (69), 364 (2), 335 (100), 334 (100), 288 (46), 283 (42), 236 (92).

The same reaction carried out on the enamine 6 led to the isolation of 14 (0.20 g, 70% yield), [3aR*-(1R*(or S*),2R*(or S*),3aα,4β,6aα)]-4-hydroxy-4-methyl-5-(4-morpholinyl)-3a-nitro-6-(2-nitro-cyclopentyl)-1,2,3,3a,4,5-hexahydro-pentalene, m.p. 102 °C (Found: C, 56.45; H, 7.08; N, 11.12. $C_{18}H_{27}N_3O_6$ requires: C, 56.68; H, 7.13; N, 11.02%); IR, ν_{max}, cm^{-1}: 3540 (OH), 1670 (C=C), 1540, 1530, 1365, 1355 (NO_2), 1110 (C-O-C); ^1H NMR, δ: 5.3 (m, 1 H, $CHNO_2$), 3.7 (t, 4 H, CH_2OCH_2), 3.0 (m, 6 H), 2.5-1.5 (m, 13H), 1.4 ppm (s, 3 H, Me); ^{13}C NMR, δ: 149.1 (s), 132.1 (s), 107.6 (s), 89.9 (d), 83.5 (s), 67.2 (2 t), 57.8 (2 t), 49.6 (d), 44.9 (d), 34.1 (t), 31.7 (t), 30.8 (t), 29.2 (t), 24.8 (q), 23.7 (t), 23.9 ppm (t); MS: M^+ 381 (50), 364 (2), 335 (72), 288 (42), 283 (60), 236 (44), 43 (100).

X-Ray Crystal Structure Analysis of 10

Well shaped colourless single crystals were obtained by slow evaporation from ether-n-pentane solution. Cell parameters, determined from Weissenberg photographs, were refined from 20 randomly selected reflections in the range $12<\vartheta<20°$ obtained using the CAD-4 automatic routines. All data processing was performed on a PDP11/44 computer using the Enraf-Nonius SDP program library.[11] Neutral atom scattering factors were taken from the literature.[12] The structure was solved by direct methods (MULTAN) which allowed location of the independent O, N, and C atoms. Hydrogen atoms were located at calculated positions and they were held fixed (β = 7 $Å^2$) during the refinement. Full-matrix least-squares refinement using anisotropic thermal parameters converged to the final R factors shown in Table 1. Crystal data are given in Table 1 and final atomic positional coordinates with the e.s.d.'s in parentheses are listed in Table 2. Listing of anisotropic temperature factors, fractional coordinates and structure factor amplitudes are available as supplementary material.[14]

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