[3 + 2] Carbocyclization Reactions of Linear α-Ketoenamines with Conjugated Nitroolefins

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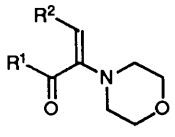
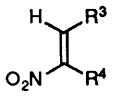
Three linear α-ketoenamines were allowed to react with a series of cyclic and acyclic nitroolefins, to yield aminocyclopentene derivatives with high diastereoselectivity. The corresponding polysubstituted nitrocyclopentanones were obtained by hydrolysis, which also proceeded with a high degree of diastereoselectivity when the system was prochiral.

The α-ketoenamine **1** derived from diacetyl and morpholine has recently been shown to react with conjugated nitroolefins to yield substituted five-membered rings,[1,2] obtained as products of [3 + 2] carbocyclization reactions with a high degree of diastereoselectivity.† Continuing our research into this type of annulation reactions, we have examined the behaviour of the α-ketoenamines **2**, **3** and **4** towards the electrophilic olefins **5**, with the purpose of making a comparison between the system **1** and these latter substrates, which present an increasing complexity in their structure; compounds **3** and **4** in particular are substituted also at their enamine β-carbon atom.



1; R^1 = Me, R^2 = H
2; R^1 = Et, R^2 = H
3; R^1 = Et, R^2 = Me
4; R^1 = Ph, R^2 = Ph

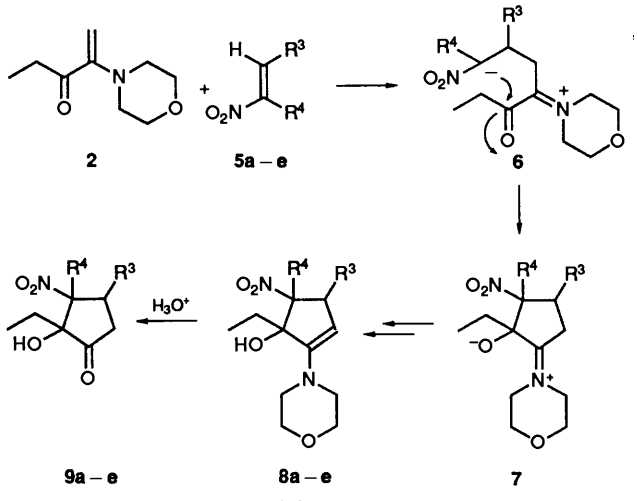


5 a; R^3 = Me, R^4 = H
b; R^3 = H, R^4 = Me
c; R^3 = Ph, R^4 = H
d; R^3 = Ph, R^4 = Me
e; R^3 = Me, R^4 = Ph
f; R^3, R^4 = $(CH_2)_3$
g; R^3, R^4 = $(CH_2)_4$

Substituents **a** – **g** are used throughout.

Results and Discussion

The α-ketoenamine **2**‡ derived from pentane-2,3-dione, was allowed to react with the nitroalkenes **5**. The reactions were carried out in the absence of solvent, as is usual for α-ketoenamines,[4] in a range of temperatures varying from −70 to 0 °C, depending on the reactivity of the electrophilic counterpart. The reactions with the acyclic nitroolefins **5a–e** afforded the cyclopentenyl–morpholino derivatives **8a–e** always as single diastereoisomers and in quantitative yield. It is evident that the diastereoselectivity arose from the ring-closure step, which involved the attack of the carbanion onto the carbonyl carbon atom in the dipolar intermediate **6** (Scheme 1). This



Scheme 1

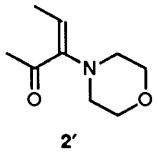
result was further confirmed by obtaining the corresponding cyclopentanone derivatives **9a–e**, also as single diastereoisomers. In fact no chiral centre was involved in the hydrolyses of the aminocyclopentenyl derivatives **8a–e**. The configurations of their chiral centres have not been assigned as yet, as the stereochemistry of five-membered rings cannot be assigned unambiguously from coupling constants.

The aminocyclopentene **8b** was shown to be unstable. Running its ^1H NMR spectrum in $CDCl_3$ at regular intervals showed that it underwent a retro nitro-aldol type reaction into the corresponding Michael-type adduct **10b**, whose hydrolysis, carried out at pH 2, yielded the corresponding open-chain nitrodiketone **11b** (Scheme 2).

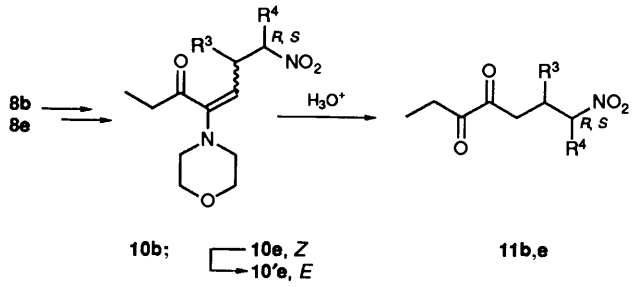
When the nitroolefin used was 1-nitro-1-phenylprop-1-ene **5e** the reaction at first took a different course; carrying it out at −78 °C, a [4 + 2] heterocyclization reaction occurred, leading to a 1,2-oxazine *N*-oxide system **12** as a product of kinetic control (Scheme 3), whose formation had not been observed in the analogous reaction of the α-ketoenamine **1**.[1] The 1,2-oxazine *N*-oxide derivative was identified only by its IR spectrum, characterized by the C=O stretching band at ν 1720 cm^{-1} and the signal relative to the Ph–C=N^+–O^- system at 1575 and 1560 cm^{-1};[5] no absorption band corresponding to a

† Similar behaviour had already been found by Pocar and co-workers[3] for the 2,3-diaminobuta-1,3-diene obtained from diacetyl and morpholine in ratio 1:2, in its reactions with nitroolefins. However, the diastereoselectivity observed was much less.

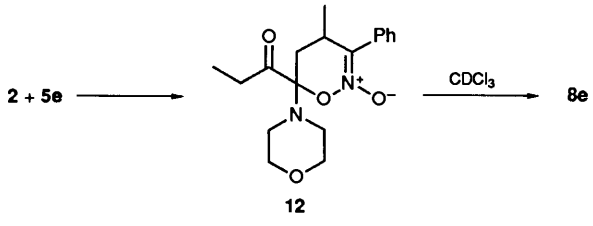
‡ The regioisomer **2'** (12%) was also detected in the NMR spectrum [δ_H 4.8 (q, C*H*CH_3), 2.3 (s, MeCO) and 1.7 (d, *J* 7 Hz, C*H*CH_3)]; however, it did not react within the reaction time of the main isomer **2**, as proved by the ^1H NMR analysis of the crude products.



2'



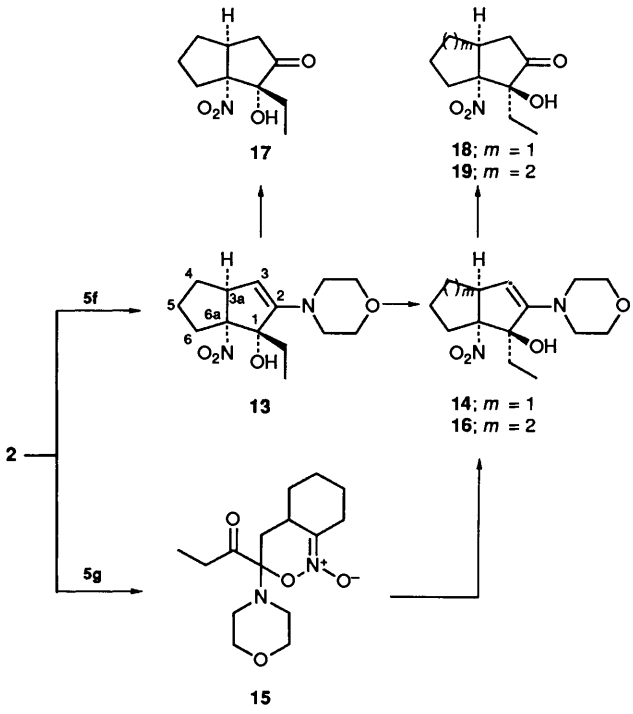
Scheme 2



Scheme 3

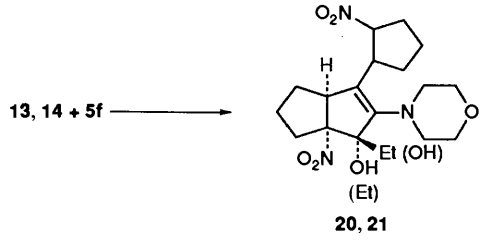
free nitro group was observed. In solution of $CDCl_3$, however, the heterocyclic system was immediately converted into the corresponding cyclopentenyl derivative **8e** as a single diastereoisomer, this transformation occurring by nucleophilic ring fission[6] into the dipolar intermediate **6**, followed by recyclization to the betaine-system of the type **7** (Scheme 1). Furthermore, the aminocyclopentene itself was not stable in $CDCl_3$, as it opened into a 1:1 mixture of linear Michael-type adducts in *Z* and *E* configuration **10e**, **10'e** each as a diastereoisomeric pair, differing in the configuration of the carbon atom bearing the nitro group. The enamines **10e** which were attributed the less stable *Z* configuration, slowly isomerized into the *E* diastereoisomers **10'e** completely. The geometric isomerization could be followed also by IR spectroscopy, the C=O stretching frequency of the two isomers absorbing at *v* 1680 and 1695 cm^{-1} respectively. This frequency difference is probably the result of a balance between the two possible types of conjugation; *i.e.* C=C–C=O and N–C=C. In fact it is the former which operates as the latter is inhibited by the strong steric interaction between the base and the nitroalkylated chain. Acidic hydrolysis of the mixture **10e**, **10'e** furnished the corresponding acyclic nitro diketone **11e**.

The α-ketoenamine **2** was then allowed to react with both the cyclic nitroalkenes **5f** and **5g**, affording the hexahydropentalene **13** and the 1,2-oxazine *N*-oxide **15** respectively, as products of kinetic control (Scheme 4). The first compound **13** isomerized, either in $CDCl_3$ solution in 72 h or more slowly in the solid state, into the more stable diastereoisomer **14**, while the heterocyclic system **15** underwent nucleophilic ring fission[6] to give an aminohexahydroindene **16** as the product of thermodynamic control. A remarkable result was the ease with which the hexahydropentalenone derivatives **17** and **18** were obtained quantitatively and extremely quickly at pH 2, at room temp. by hydrolysis of **13** and **14** respectively.* This is surprising because the hydrolysis of both the hexahydropentalenes derived from the ketoenamine **1** did not proceed under the same conditions.[2] Instead a partial cycloreversion into the reactants



Scheme 4

occurred, leading eventually to a pair of double addition products analogous to **20** and **21**, which were quantitatively obtained from **13** and **14** by reaction with an equimolar amount of nitrocyclopentene (Scheme 5).

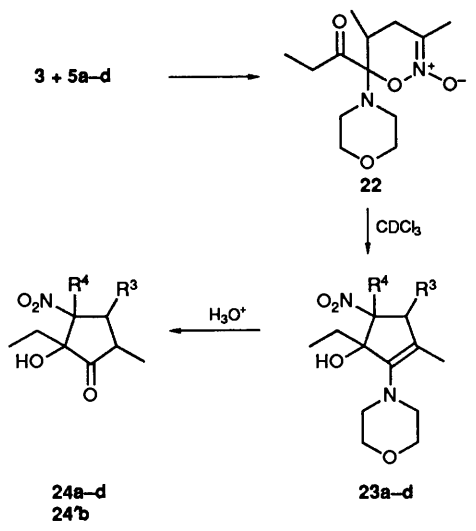


Scheme 5

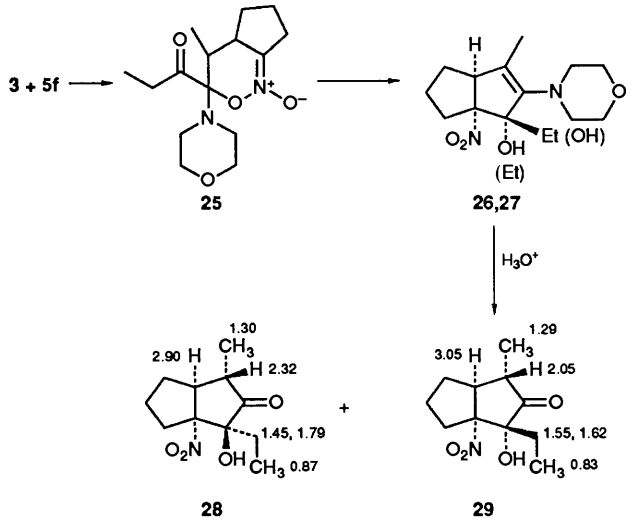
The stereochemical results obtained in these reactions, which always gave diastereoisomerically pure compounds, led us to extend our studies to the α-ketoenamines **3** and **4**, in which the enamine β-carbon atom is substituted by a methyl and a phenyl group respectively. The purpose was to verify whether in these cases in which the steric situation is more hindered the [3 + 2] carbocyclization was again possible and in this case whether the ring closure could proceed with a high degree of diastereoselectivity. A further point of interest was to verify the degree of diastereoselectivity in the hydrolyses of the tetrasubstituted enamine intermediates, in which the centre of protonation is prochiral.

The α-ketoenamine **3** was easily prepared from hexane-3,4-dione by the method of White and Weingarten.[7] The reactions with the nitroalkenes were carried out under the usual conditions. Two of them, namely **5e** and **5g**, failed to react, whereas with the other nitroolefins **5a–d** the corresponding aminocyclopentenyl derivatives **23a–d** were formed. They could be identified only spectroscopically, with the exception of **23b** which was isolated as a crystalline product. It could be shown however that formation of the latter compound was preceded by formation of the corresponding 1,2-oxazine *N*-oxide derivative **22** (Scheme 6), on the basis of IR spectroscopic evidence. Also in the cases in which the reaction products could not be isolated, namely with **5a**, **c**, **d**, the reactions occurred with a high

* The configurations of the chiral centres in compounds **13**, **14** and **16** were assigned by comparing their ^1H NMR spectra with those of the analogous compounds derived from the substrate **1**.[2] They were practically superimposable. The same configurations were then attributed to the corresponding ketols **17**, **18** and **19**, as under the hydrolysis conditions used, the chiral centres were not involved.



Scheme 6

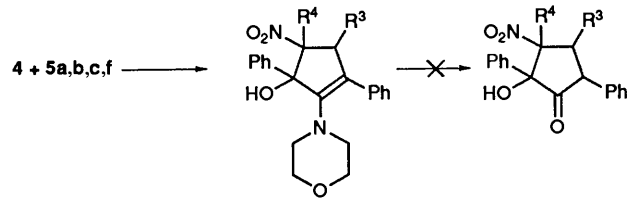


Scheme 7

diastereoselectivity, as the hydrolyses of the crude products always furnished the corresponding cyclopentanone derivatives **24a**, **c**, **d** as single diastereoisomers, thus indicating that hydrolyses too were diastereoselective. In contrast, hydrolysis of **23b** led to a 2:1 mixture of cyclopentanones **24b** and **24'b** as determined by ^{1}H NMR spectroscopic analysis. The two diastereoisomers are likely to differ in the configuration at C-2 as a consequence of a non-diastereoselective protonation at the β-carbon atom in the system **23b**. Since in the other cases the hydrolyses were diastereoselective, this lack of diastereoselectivity can be attributed to the absence of a substituent at C-3. An attempted equilibration of the systems **24** under acidic conditions failed, leading to mixtures of unidentified products, which are likely to be open chain, since their IR spectra showed absorption at ν 1720–1700 cm^{-1}, whereas stretching bands at ν 1750 cm^{-1} relative to the C=O of the cyclopentanone were absent. The reaction with nitrocyclopentene **5f** afforded the corresponding 1,2-oxazine *N*-oxide system **25** as product of kinetic control, isolated as a single diastereoisomer. This product turned out to be quite stable both in the solid state and in $CHCl_3$ solution, its rearrangement into the hexahydropentalene system **26**, **27** as a pair of diastereoisomers taking 1 week to complete. This mixture however could not be separated by flash chromatography, since it underwent easy hydrolysis on silica gel. The hydrolysis was therefore performed on the mixture in chloroform–water, at pH 5, affording the two diastereoisomers **28** and **29**.

The stereochemistry depicted in Scheme 7 for compounds **28** and **29** are based on the chemical shift values of the substituents which are also reported in Scheme 7. In **28** the methylene protons are deshielded by the effect of the nitro group, whereas in **29** they resonate much closer. Therefore, the *cis* and *trans* relationships were assigned to these groups in **28** and **29** respectively. The methyl group at C-2 and the nitro group are likely to be on the same side, since the former resonates at almost the same value in both compounds (1.30 and 1.29 ppm respectively), and at lower field than that of another isomer, detected in the hydrolysis mixture (8%) and not fully characterized. In this compound the methyl group resonates at 1.04 ppm, a value which favours a *trans* relationship between the nitro group and the methyl group itself.

The last system we have taken into account was the α-keto-enamine **4**.[8] The presence of two phenyl groups on both the carbonyl and the β-carbon atom severely affected the reactivity of this substrate. In fact, it failed to react with the more hindered nitroolefins **5d**, **e**, **g**. Only with **5a**, **b**, **c**, **f** did the reactions proceed in the unusual way, leading to the expected aminocyclopentenyl derivatives **30a**, **b**, **c**, **f** (Scheme 8).



Scheme 8

Unfortunately, these enamine systems could not be hydrolysed to the corresponding cyclopentanone derivatives **31a**, **b**, **c**, **f** even on heating, probably because the presence of a bulky substituent at the β-carbon atom inhibited its protonation.

Experimental

M.p.s were determined with a Büchi apparatus and are uncorrected. IR spectra were recorded in Nujol mulls, unless otherwise stated, on a Perkin-Elmer 1320 spectrometer. ^{1}H NMR spectra were measured on Varian 360 A (60 MHz), Varian VXR (300 MHz) or a Bruker XL (200 MHz), using deuteriochloroform as solvent, unless otherwise stated, and tetramethylsilane as internal standard; ^{13}C NMR were recorded on a Bruker WP-80 (20.1 MHz). *J* Values are given in Hz. Electron impact mass spectra were obtained on a VG 7070 spectrometer at 70 eV. TLC were performed on Whatman K6F silica gel plates. Flash chromatography was run on silica gel 230–400 mesh ASTM. Kieselgel 60, Merck. Light petroleum refers to that fraction with b.p. 40–70 °C and ether to diethyl ether.

Synthesis of the Reactants.—*2-Morpholinopent-1-en-3-one* **2**. This was prepared from pentane-2,3-dione by a literature method;[7] as a yellow oil (30%), b.p. 88 °C/1 mmHg; ν_{max}/cm^{-1} 1690 (C=O), 1590 (C=C) and 1110 (COC); δ_H(60 MHz) 5.1 (1 H, d, *J* 2, C=CH), 4.7 (1 H, d, *J* 2, C=CH), 3.8 [4 H, m, $(CH_2)_2O$], 2.8 [4 H, m, $(CH_2)_2N$], 2.6 (2 H, q, *J* 7, CH_2CH_3) and 1.1 (3 H, t, *J* 7, CH_3CH_2); δ_C 201.7 (s), 155.5 (s), 98.7 (t), 66.3 (2t), 49.4 (2t), 32.8 (t) and 8.3 (q); *m/z* 169.110 50 (M$^+$, 11%, Calc. for $C_9H_{15}NO_2$: *M*, 169.110 27), 138 (1), 126 (25), 112 (58), 100 (15), 86 (27), 68 (19), 57 (61) and 43 (100).

4-Morpholinohex-4-en-3-one **3**. This was prepared from

hexane-3,4-dione by a literature method;[7] as a pale yellow oil (25%), b.p. 77 °C/0.1 mmHg; ν_{max}/cm^{-1} 1690 (C=O), 1620 (C=C) and 1120 (COC); δ_H(60 MHz) 4.9 (1 H, q, *J* 7, CH=C), 3.8 [4 H, m, $(CH_2)_2O$], 2.7 [6 H, m, $(CH_2)_2N$ and CH_2CH_3], 1.7 (3 H, d, *J* 7, CH_3CH) and 1.1 (3 H, t, *J* 7, CH_3CH_2); δ_C 206.3 (s), 150.6 (s), 106.9 (d), 67.1 (2t), 50.5 (2t), 35.3 (t), 13.3 (q) and 8.3 (q); *m/z* 183.124 50 (M^+, 19%, Calc. for $C_{10}H_{17}NO_2$: *M*, 183.125 92), 154 (18), 140 (4), 126 (100), 98 (13), 86 (27), 70 (26), 55 (34) and 43 (53).

2-*Morpholino*-1,3-*diphenylprop*-1-*en*-3-*one* **4**.[8] This had m.p. 96–98 °C (lit.,[8] 94–96 °C) (Found: C, 77.8; H, 6.45; N, 4.8. Calc. for $C_{19}H_{19}NO_2$: C, 77.79; H, 6.53; N, 4.77%); ν_{max}/cm^{-1} 1660 (C=O), 1595 (C=C) 1115 (COC) (lit.,[8] 1664, 1597 and 1120); δ_H(60 MHz) 8.0 (2 H, m, *o*-ArH), 7.3 (3 H, m, *m*- and *p*-ArH), 7.0 (5 H, s, Ph), 5.9 (1 H, s, CH=C), 3.8 [4 H, m, $(CH_2)_2O$] and 2.9 [4 H, m, $(CH_2)_2N$]; δ_C 196.1 (s), 146.9 (s), 135.8 (s), 135.3 (s), 132.8 (d), 128.6 (d), 127.6 (d), 127.2 (d), 127.1 (d), 124.9 (d), 107.0 (d), 65.5 (2t) and 47.6 (2 t); *m/z* 293 (M^+, 73%), 207 (15), 188 (100), 105 (41), 86 (94) and 77 (59).

1-*Nitropropene* **5a** *and* 2-*nitropropene* **5b**. These were prepared by a literature method,[9] β-nitrostyrene **5c** was used as purchased (Aldrich), 2-nitro-1-phenylpropene **5d**,[10] 1-nitro-1-phenylpropene **5e**,[5] 1-nitrocyclopentene **5f**,[11] and 1-nitrocyclohexene **5g**,[11] were prepared by literature methods.

Reaction of **2** *with* 1-*Nitropropene* **5a**.—The nitroolefin **5a** (0.5 g, 5.9 mmol) was added to the α-ketoenamine **2** (1.0 g, 5.9 mmol) at −30 °C. After 2 h at −18 °C a solid product was separated from the crude mixture by addition of a small amount of dry ether and was identified as 1-*ethyl*-4-*methyl*-2-*morpholino*-5-*nitrocyclopent*-2-*enol* **8a** (1.2 g, 80%), m.p. 134 °C (Found: C, 56.1; H, 8.0; N, 10.9. $C_{12}H_{20}N_2O_4$ requires C, 56.24; H, 7.87; N, 10.93%); ν_{max}/cm^{-1} 3330 (OH), 1625 (C=C), 1540, 1370 (NO_2) and 1110 (COC); δ_H(C_6D_6; 60 MHz) 4.5 (1 H, d, *J* 6.5, $CHNO_2$), 4.2 (1 H, d, *J* 4, C=CH), 3.5 [5 H, m, $(CH_2)_2O$ and OH], 2.9 (2 H, m, CH_2N), 2.3 (2 H, m, CH_2N), 2.1–1.8 (3 H, m, 4-H and CH_2CH_3), 0.9 (3 H, t, *J* 7, CH_3CH_2) and 0.8 (3 H, d, *J* 6, 3-Me); *m/z* 256 (M^+, 30%), 238 (M − H_2O, 10), 210 (M − NO_2, 49), 209 (M − HNO_2, 63), 195 (35), 184 (63), 180 (70), 164 (16), 151 (30), 138 (40), 123 (32), 114 (40), 91 (23), 86 (48), 80 (35), 70 (44), 57 (83), 53 (70) and 41 (100).

The aminocyclopentene **8a** (0.5 g, 1.9 mmol) was dissolved in methanol and the solution acidified to pH 2 with HCl (10%); after 2 h at room temp. the solvent was removed under reduced pressure and the residue diluted with water and extracted with ether. The extract was washed with saturated aqueous $NaHCO_3$ and water, dried (Na_2SO_4), and evaporated to afford an oil. Flash chromatography on silica gel using ethyl acetate–light petroleum (1:9) as eluent led to 2-*ethyl*-2-*hydroxy*-4-*methyl*-3-*nitrocyclopentanone* **9a** (0.22 g, 62%), m.p. 102 °C from chloroform–hexane (Found: C, 51.35; H, 7.1; N, 7.4. $C_8H_{13}NO_4$ requires C, 51.33; H, 7.00; N, 7.48%); ν_{max}/cm^{-1} 3350 (OH), 1760 (C=O), 1540 and 1365 (NO_2); δ_H(300 MHz) 4.88 (1 H, d, *J* 4, $CHNO_2$), 3.0 (1 H, br s, OH), 2.77–2.63 (2 H, m, CH_2CO), 2.30 (1 H, m, 4-H), 1.68, 1.58 (2 H, each dq, each ^2J 14.7 and ^3J 7.0, CH_2CH_3), 1.17 (3 H, d, *J* 6.6, 4-Me) and 0.96 (3 H, t, *J* 7.0, CH_3CH_2); δ_C 213.0 (s), 94.6 (d), 83.2 (s), 38.2 (t), 29.7 (d), 28.7 (t), 28.1 (q) and 15.3 (q); *m/z* 130 (6%), 99 (31), 81 (6), 69 (21), 57 (100), 43 (27) and 41 (24).

Reaction of **2** *with* 2-*Nitropropene* **5b**.—The nitroolefin **5b** (0.50 g, 5.9 mmol), was added to the α-ketoenamine **2** (1 g, 5.9 mmol) at −30 °C. After 2 h at −20 °C as a crystalline product was separated and identified as 1-*ethyl*-5-*methyl*-2-*morpholino*-5-*nitrocyclopent*-2-*enol* **8b** (1.40 g, 92%), m.p. 90 °C (Found: C, 56.3; H, 7.95; N, 10.85. $C_{12}H_{20}N_2O_4$ requires C, 56.24; H, 7.87; N, 10.83%); ν_{max}/cm^{-1} 3395 (OH), 1630 (C=C), 1530, 1360 (NO_2) and 1105 (COC); δ_H(60 MHz) 4.8 (1 H, m, C=CH), 3.7 [4 H, m, $(CH_2)_2O$], 3.3–2.5 [7 H, m, $(CH_2)_2N$, CH_2CO, OH], 1.8 (2 H, q, *J* 7, CH_2CH_3), 1.7 (3 H, s, 4-Me) and 1.0 (3 H, t, *J* 7, CH_3CH_2); δ_C 149.5 (s), 101.0 (d), 99.2 (s), 85.8 (s), 66.8 (2t), 49.8 (2t), 40.2 (t), 29.2 (t), 21.0 (q) and 8.7 (q); *m/z* 256 (M^+, 10%), 239 (M − OH, 5), 227 (6), 210 (M − NO_2, 13), 184 (22), 180 (17), 156 (5), 140 (4), 128 (9), 114 (11), 99 (11), 86 (23), 77 (20), 57 (100) and 40 (67).

In $CDCl_3$ the aminocyclopentene **8b** converted within 24 h into the acyclic nitroalkylated α-ketoenamine 4-morpholino-7-nitrooct-4-en-3-one **10b**, which was not isolated; ν_{max}($CDCl_3$)/cm^{-1} 1695 (C=O), 1640 (C=C), 1540, 1370 (NO_2) and 1110 (COC); δ_H(60 MHz) 4.7 (2 H, m, $CHNO_2$ and C=CH), 3.8 [4 H, m, $(CH_2)_2O$], 3.5–3.1 [6 H, m, $(CH_2)_2N$ and CH_2–CH=C], 1.8 (2 H, q, *J* 7, CH_2CH_3), 1.6 (3 H, d, *J* 7, CH_3CH) and 1.1 (3 H, t, *J* 7, CH_3CH_2). Its hydrolysis at pH 5 under the usual conditions furnished, after purification of flash chromatography using ethyl acetate–light petroleum (1:9) as eluent, the corresponding acyclic 1,2-diketone identified as 7-*nitrooctane*-3,4-*dione* **11b**, yellow oil; ν_{max}(neat)/cm^{-1} 1710 (C=O) 1550 and 1360 (NO_2); δ_H(60 MHz) 4.7 (1 H, m, $CHNO_2$), 2.9–2.7 (4 H, m), 2.0 (2 H, m), 1.6 (3 H, d, *J* 7, CH_3CH) and 1.1 (3 H, t, *J* 7, CH_3CH_2); *m/z* 130.050 45 (M − C_3H_5O, 1%, $C_5H_8NO_3$ requires 130.050 41) 109 (2), 83 (2), 69 (1) and 57 (100).

The aminocyclopentene **8b** (0.40 g, 1.6 mmol) was hydrolysed under the same conditions as above, to yield, after work-up, the corresponding ketone identified as 2-*ethyl*-2-*hydroxy*-3-*methyl*-3-*nitrocyclopentanone* **9b** (0.22 g, 77% yield), m.p. 98 °C from chloroform–hexane (Found: C, 51.35; H, 7.1; N, 7.4. $C_8H_{13}NO_4$ requires C, 51.33; H, 7.00; N, 7.48%); ν_{max}/cm^{-1} 3350 (OH), 1760 (C=O), 1540 and 1370 (NO_2); δ_H(300 MHz) 2.99 (1 H, s, OH), 2.72 (1 H, m), 2.51 (2 H, m), 2.14 (1 H, m), 1.73, 1.45 (each 1 H, each dq, each ^2J 14.4 and ^3J 7.0, CH_2CH_3), 1.68 (3 H, s, 3-Me) and 0.85 (3 H, t, *J* 7.0, CH_3CH_2); δ_C 213.0 (s), 94.6 (s), 83.7 (s), 38.2 (t), 29.7 (t), 28.7 (t), 28.1 (q) and 15.3 (q); *m/z* 141 (M − NO_2, 7%), 140 (M − HNO_2, 9), 130 (17), 99 (100), 83 (23), 69 (41) and 57 (90).

Reaction of **2** *with* β-*Nitrostyrene* **5c**.—The nitroolefin **5c** (0.88 g, 5.9 mmol) was added to the α-ketoenamine **2** (1.0 g, 5.9 mmol) at −40 °C; after 12 h at −18 °C treatment with ether–hexane afforded 1-*ethyl*-2-*morpholino*-5-*nitro*-4-*phenylcyclopent*-2-*enol* **8c** (1.78 g, 95%), m.p. 132–133 °C (Found: C, 64.3; H, 6.85; N, 8.7. $C_{17}H_{22}N_2O_4$ requires C, 64.13; H, 6.97; N, 8.80%); ν_{max}/cm^{-1} 3310 (OH), 1620 (C=C), 1535, 1370 (NO_2) and 1105 (COC); δ_H(C_6D_6; 60 MHz) 7.2 (5 H, s, Ph), 4.7 (2 H, br s, $CHNO_2$ and CHPh), 4.3 (1 H, d, *J* 1.5, CH=C), 3.4 [4 H, m, $(CH_2)_2O$], 2.8 [5 H, m, $(CH_2)_2N$ and OH], 1.7 (2 H, q, *J* 7, CH_2CH_3) and 0.7 (3 H, t, *J* 7, CH_3CH_2); δ_C 150.8 (s), 132.2 (s), 129.0 (d), 127.6 (d), 127.1 (d), 107.1 (d), 96.0 (d), 85.0 (s), 66.7 (2t), 50.0 (2t), 48.4 (d), 29.9 (t) and 8.7 (q); *m/z* 318 (M^+, 23%), 271 (M − HNO_2, 100), 242 (94), 226 (20), 212 (42), 184 (76), 128 (50), 115 (56), 91 (42), 77 (41) and 57 (56).

Hydrolysis of the compound **8c** (0.60 g, 1.9 mmol) carried out at pH 2 led to 2-*ethyl*-2-*hydroxy*-3-*nitro*-4-*phenylcyclopentanone* **9c** (0.32 g, 67%), m.p. 128 °C from chloroform–hexane (Found: C, 63.1; H, 5.4; N, 5.55. $C_{13}H_{15}NO_4$ requires C, 63.15; H, 5.30; N, 5.66%); ν_{max}/cm^{-1} 3425 (OH), 1750 (C=O), 1550 and 1370 (NO_2); δ_H(60 MHz) 7.3 (5 H, s, Ph), 5.0 (1 H, d, *J* 8.5, $CHNO_2$), 4.2 (1 H, ddd, $J_{3,4}$ 8.5, J_{AX} 8.2, J_{BX} 11.3, CHPh), 3.0, 2.6 (each 1 H, dq, part AB of an ABX system, J_{AB} 18.5, J_{AX} 8.2, J_{BX} 11.3, CH_2CO), 1.75 (3 H, q and br s, CH_2CH_3 and OH) and 0.9 (3 H, t, *J* 7, CH_3CH_2); δ_C 212.3 (s), 134.1 (s), 129.4 (d), 128.4 (d), 127.4 (d), 95.3 (d), 83.4 (s), 40.8 (d), 35.7 (t), 28.4 (t) and 7.1 (q); *m/z* 231 (M − H_2O, 5%), 192 (79), 161 (22), 145 (26), 131 (87), 117 (22), 115 (15), 103 (48), 91 (20), 77 (42), 57 (100), 51 (18) and 43 (11).

Reaction of **2** *with* 2-*Nitro*-1-*phenylpropene* **5d**.—The

nitroolefin **5d** (1.15 g, 7.1 mmol) was added to the ketoenamine **2** (1.2 g, 7.1 mmol) at room temp. After 24 h treatment of the crude product with ether afforded 1-*ethyl*-5-*methyl*-2-*morpholine*-5-*nitro*-4-*phenylcyclopent*-2-*enol* **8d** (2.1 g, 90%), m.p. 133 °C (Found: C, 64.9; H, 7.1, N, 7.6. $C_{18}H_{24}N_2O_4$ requires C, 65.04; H, 7.28; N, 8.43%); ν_{max}/cm^{-1} 3350 (OH), 1615 (C=C), 1525, 1370 (NO_2) and 1105 (COC); δ_H(60 MHz) 7.2 (5 H, m, Ph), 5.1 (1 H, d, *J* 1.5, C=CH), 4.9 (1 H, d, *J* 1.5, C*H*Ph), 3.8 [4 H, m, $(CH_2)_2O$], 3.4–2.6 [5 H, m and br s, $(CH_2)_2N$ and OH], 1.9 (2 H, q, *J* 7, CH_2CH_3), 1.2 (3 H, s, 4-Me) and 1.0 (3 H, t, *J* 7, CH_3CH_2); δ_C 149.7 (s), 138.9 (s), 129.5 (d), 128.4 (d), 127.6 (d), 103.0 (s), 102.6 (d), 86.8 (s), 66.8 (2t), 49.5 (2t), 48.7 (d), 31.0 (t), 19.9 (q) and 8.6 (q); *m*/*z* 332 (M^+, 10%), 286 (M − NO_2, 29), 259 (100), 184 (70), 156 (14), 142 (17), 129 (26), 116 (32), 106 (20), 91 (30), 77 (32) and 57 (56).

Hydrolysis of the compound **8d** (0.80 g, 2.4 mmol) carried out under the same conditions as above, afforded the corresponding ketone 2-*ethyl*-2-*hydroxy*-3-*methyl*-3-*nitro*-4-*phenylcyclopentanone* **9d** (0.40 g, 67%), m.p. 119 °C from chloroform–hexane (Found: C, 64.1; H, 6.3; N, 5.1. $C_{14}H_{17}NO_4$ requires C, 63.87; H, 6.51; N, 5.32%); ν_{max}/cm^{-1} 3460 (OH), 1740 (C=O), 1530 and 1370 (NO_2); δ_H(60 MHz) 7.3 (5 H, m, Ph), 3.6 (1 H, dd, part X of an ABX system, J_{AX} 12.0, J_{BX} 8.0, C*H*Ph), 3.1, 2.9 (each 1 H, dq, part AB of an ABX system, J_{AB} 20, J_{AX} 12, J_{BX} 8.0, CH_2CO), 2.5 (1 H, br s, OH), 1.8 (2 H, q, *J* 7, CH_2CH_3), 1.3 (3 H, s, 3-Me) and 0.8 (3 H, t, *J* 7, CH_3CH_2); δ_C 209.9 (s), 134.6 (s), 128.4 (d), 127.9 (d), 127.3 (d), 97.1 (s), 84.4 (s), 40.9 (d), 36.9 (t), 25.3 (t), 15.5 (q) and 5.9 (q); *m*/*z* 176 (10%), 160 (9), 132 (80) 91 (51), 77 (54) and 57 (100).

Reaction of **2** *with* 1-*Nitro*-1-*phenylpropene* **5e**.—The nitroolefin **5e** (0.96 g, 5.9 mmol) was added to the α-ketoenamine **2** (1.0 g, 5.9 mmol) at −70 °C; after 12 h at −20 °C a crystalline product was isolated and identified as 5,6-*dihydro*-4-*methyl*-6-*morpholino*-3-*phenyl*-6-*propionyl*-4H-1,2-*oxazine* N-*oxide* **12** (1.65 g, 83%), m.p. 75 °C (Found: C, 64.9; H, 7.1, N, 7.6; $C_{18}H_{24}N_2O_4$ requires C, 65.04; H, 7.28; N, 8.43%); ν_{max}/cm^{-1} 1720 (C=O), 1575, 1560 (Ph–C=$\overset{+}{N}$–$\overset{-}{O}$) and 1100 (COC); *m*/*z* 332 (M^+, 0.2%), 285 (M − HNO_2, 15), 256 (18), 196 (100), 184 (50), 180 (12), 150 (10), 138 (25), 128 (34), 115 (20), 103 (50), 91 (71), 77 (20), 70 (25) and 57 (78).

In $CDCl_3$ **12** was immediately converted into 1-*ethyl*-4-*methyl*-2-*morpholino*-5-*nitro*-5-*phenylcyclopent*-2-*enol* **8e**, m.p. 68 °C (Found: C, 65.1; H, 7.3; N, 8.3. $C_{18}H_{24}N_2O_4$ requires C, 65.04; H, 7.28; N, 8.43%); ν_{max}/cm^{-1} 3490 (OH), 1630 (C=C), 1530, 1370 (NO_2) and 1100 (COC); δ_H(60 MHz) 7.5 (5 H, s, Ph), 4.4 (1 H, d, *J* 1.5, CH=C), 3.7 [5 H, m, $(CH_2)_2O$ and OH], 3.1 [4 H, m, $(CH_2)_2N$], 2.7 (1 H, m, 4-H), 1.3 (2 H, q, *J* 7, CH_2CH_3), 1.1 (3 H, d, *J* 7, 4-Me) and 0.6 (3 H, t, *J* 7, CH_3CH_2); *m*/*z* 332 (M^+, 8%), 286 (M − NO_2, 20), 259 (42), 184 (20), 156 (14), 129 (26), 116 (31), 106 (18), 91 (30) and 57 (100). Within 4 h compound **8e** had been converted into the corresponding acyclic nitroalkylated enamine as an inseparable mixture of *Z*- and *E*-isomers **10e** and **10′e** (ratio approximately 4:6 by ^{1}H NMR spectroscopy); both isomers were present as a pair of diastereoisomers (ratio 1:1, by ^{1}H NMR spectroscopy), differing for the configuration at C-7; they were attributed the structure of (6R*, 7R* *and* S*)-(E),(Z)-6-*methyl*-4-*morpholino*-7-*nitro*-7-*phenylhept*-4-*en*-3-*one*; ν_{max}(neat)/cm^{-1} 1695, 1680 (C=O), 1620 (C=C), 1550, 1380, 1360 (NO_2) and 1110 (COC); δ_H 7.5 (5 H, m, Ph), 6.2, 5.8 [0.4 H, each d, rel. int. 1:1, each *J* 10, (*Z*)-$CHNO_2$], 5.5, 5.3 [0.4 H, each d, rel. int. 1:1, each *J* 1.5, (*Z*)–C=H], 5.3, 5.1 [0.6 H, each d, rel. int. 1:1, each *J* 1.5, (*E*)-C=CH], 4.6, 4.3 [0.6 H, each d, rel. int. 1:1, each *J* 10, (*E*)-$CHNO_2$], 3.8 [4 H, m, $(CH_2)_2O$], 2.9–2.3 [7 H, m, $(CH_2)_2N$, CH_3CH, CH_2CH_3], 1.3–0.9 [6 H, m, (*E*)- and (*Z*)-CH_3CH and (CH_3CH_2)]. In 7 d the (*Z*)-diastereoisomer **10e** had converted completely into the (*E*)-diastereoisomer **10′e** as a 1:1 mixture of diastereoisomers differing in the configuration at C-7; ν_{max}/cm^{-1} 1695 (C=O), 1620 (C=C), 1550, 1380 (NO_2) and 1110 (COC); δ_H(60 MHz) 7.5 (5 H, m, Ph), 5.3, 5.1 (1 H, each d, rel. int. 1:1, each *J* 1.5, CH=C), 4.6, 4.3 (1 H, each d, rel. int. 1:1, each *J* 10, $CHNO_2$), 3.7 [m, 4 H, $(CH_2)_2O$], 2.8–2.4 [m, 7 H, $(CH_2)_2N$, CH_2CH_3, $CHCH_3$], 1.3–0.9 (6 H, 2t and 2d, each *J* 7, CH_3CH_2 and CH_3CH).

Hydrolysis of the mixture **10e**, **10′e**, performed at pH 2 gave a 1:1 mixture of diastereoisomers, which were not separated, of the corresponding nitroalkylated α-diketone (6R*, 7R* and S*)-6-*methyl*-7-*nitro*-7-*phenylheptane*-3,4-*dione* **11e**, m.p. 88 °C (from methanol) (Found: C, 63.9; H, 6.5; N, 5.25. $C_{14}H_{17}NO_4$ requires C, 63.87; H, 6.51; N, 5.32%); ν_{max}/cm^{-1} 1720, 1710 (C=O), 1550 and 1375 (NO_2); δ_H(60 MHz) 7.3 (5 H, m, Ph), 5.5, 5.4 (1 H, each d, rel. int. 1:1, each *J* 11, $CHNO_2$), 3.3–2.5 (5 H, m), 1.15, 1.0 (3 H, each d, each *J* 6, CH_3CH), 0.8 and 0.7 (3 H, each t, each *J* 7, CH_3CH_2); *m*/*z* 206 (23%), 176 (31), 159 (11), 131 (29), 117 (55), 107 (30), 91 (61), 77 (61) and 57 (100).

Hydrolysis of compound **8e** (0.3 g, 0.9 mmol), performed at pH 2 afforded 2-*ethyl*-2-*hydroxy*-4-*methyl*-3-*nitro*-3-*phenylcyclopentanone* **9e** (0.18 g, 78%), m.p. 188 °C from chloroform–hexane (Found: C, 63.9; H, 6.4; N, 5.25. $C_{14}H_{17}NO_4$ requires C, 63.87; H, 6.51; N, 5.32%); ν_{max}/cm^{-1} 3400 (OH), 1750 (C=O), 1530, 1370 (NO_2) and 1110 (COC); δ_H(60 MHz) 7.5 (5 H, s, Ph), 3.4 (2 H, m, 4-H and OH), 2.6 (2 H, dq, CH_2CO), 1.3 (3 H, d, *J* 6, 4-Me), 1.2 (2 H, q, CH_2CH_3) and 0.8 (3 H, t, *J* 7, CH_3CH_2); *m*/*z* 175 (M^+, 10%), 15 (11), 131 (29), 105 (67), 91 (50), 77 (68) and 57 (100).

Reaction of **2** *with* 1-*Nitrocyclopentene* **5f**.—The nitroolefin **5f** (0.67 g, 5.9 mmol) was added to the substrate **2** (1 g, 5.9 mmol) at 0 °C; after 2 h a crystalline product separated in quantitative yield and was identified as [1S*-(1α,3aα,6aα)]-1-*ethyl*-2-*morpholino*-6a-*nitro*-1,3a,4,5,6,6a-*hexahydropentalen*-1-*ol* **13** (1.78 g, 98% yield), m.p. 124 °C (Found: C, 59.6; H, 7.85; N, 9.8. $C_{14}H_{22}N_2O_4$ requires C, 59.60; H, 7.85; N, 9.92%); ν_{max}/cm^{-1} 3400 (OH), 1630 (C=C), 1535, 1370 (NO_2) and 1105 (COC); δ_H(60 MHz) 4.7 (1 H, d, *J* 2, C=CH), 4.0 (1 H, m, 3a-H), 3.8 [4 H, m, $(CH_2)_2O$], 3.2 [4 H, m, $(CH_2)_2N$], 2.9–1.6 (9 H, m) and 1.0 (3 H, t, *J* 7, CH_3CH_2); δ_C 151.6 (s), 110.4 (d), 108.7 (s), 84.5 (s), 66.7 (2t), 50.8 (2t), 49.7 (d), 35.2 (t), 31.0 (t), 27.6 (t), 25.2 (t) and 7.5 (q); *m*/*z* 282 (M^+, 12%), 236 (M − NO_2, 33), 235 (M − HNO_2, 25), 208 (30), 206 (25), 184 (62), 149 (48), 125 (54), 112 (61), 91 (49) and 57 (100).

In chloroform solution compound **13** isomerized within 72 h into its diastereoisomer [1R*-(1α,3aβ,6aβ)]-1-*ethyl*-2-*morpholino*-6a-*nitro*-1,3a,4,5,6,6a-*hexahydropentalen*-1-*ol* **14**, m.p. 110 °C (Found: C, 59.5; H, 7.9, N, 10.0. $C_{14}H_{22}N_2O_4$ requires C, 59.56; H, 7.85; N, 9.92%); ν_{max}/cm^{-1} 3400 (OH), 1620 (C=C), 1525, 1365 (NO_2) and 1115 (COC); δ_H(60 MHz) 4.3 (1 H, d, *J* 2, C=CH), 3.7 [5 H, m, 3a-H and $(CH_2)_2O$], 3.4 [5 H, m, $(CH_2)_2N$ and OH]; 1.9–1.7 (m, 8 H) and 0.9 (3 H, t, *J* 7, CH_3CH_2); δ_C 151.5 (s), 110.6 (s), 105.5 (d), 87.1 (s), 67.0 (2t), 49.5 (2t), 46.8 (d), 37.4 (t), 32.3 (t), 31.7 (t), 24.3 (t) and 9.0 (q); *m*/*z* 282 (M^+, 39%), 236 (M − NO_2, 96), 208 (78), 184 (87), 157 (31), 109 (15), 91 (67) and 57 (100).

Compound **13** (0.80 g, 2.8 mmol) was hydrolysed for 15 min at pH 2 to give, after work-up, the corresponding ketone identified as [1R*-(1α,3aα,6aα)-1-*ethyl*-1-*hydroxy*-6a-*nitro*-*octahydropentalen*-2-*one* **17** (0.53 g, 89%), m.p. 89 °C from methanol (Found: C, 56.2; H, 7.0; N, 6.7. $C_{10}H_{15}NO_4$ requires C, 56.33; H, 7.09; N, 6.57%); ν_{max}/cm^{-1} 3450 (OH), 1750 (C=O), 1540 and 1370 (NO_2); δ_H(200 MHz) 3.19 (1 H, br s, OH), 3.09 (1 H, m, 3a-H), 2.87, 2.19 (each 1 H, each dd, part AM of an AMX system, J_{AM} 18.3, J_{AX} 10.5, J_{MX} 7.0), 2.79 (1 H, m), 2.25 (1 H, m), 2.08–1.90 (4 H, m), 1.79, 1.48 (each 1 H, each dq, ^2J

14.0, ^3J 7.0, CH_2CH_3) and 0.86 (3 H, t, J 7, CH_3CH_2); δ_C 212.2 (s), 104.5 (s), 81.9 (s), 44.1 (d), 39.0 (t), 33.8 (t), 29.0 (t), 28.0 (t), 25.7 (t) and 6.9 (q); *m/z* 167 (M − NO_2, 11%), 125 (19), 109 (27), 99 (13), 81 (33), 67 (32) and 57 (100).

Hydrolysis, under the same conditions as above, of the isomer **14** (0.5 g, 1.7 mmol) led to the corresponding ketone [1R*-(1α,3aβ,6aβ)-1-*ethyl*-1-*hydroxy*-6a-*nitrooctahydropentalen*-2-*one* **18** (0.34 g, 90%), m.p. 76 °C (from methanol) (Found: C, 56.5; H, 7.05; N, 6.4. $C_{10}H_{15}NO_4$ requires C, 56.33; H, 7.09; N, 6.57%); ν_{max}/cm^{-1} 3490 (OH), 1750 (C=O), 1530 and 1350 (NO_2); δ_H(200 MHz) 3.58 (1 H, m, $w_{H/2}$ 23.9, 3a-H), 3.22 (1 H, br s, OH), 2.97, 1.97 (each 1 H, each dd, part AM of an AMX system, J_{AM} 18.9, J_{AX} 12.0, J_{MX} 5.2, 3-H), 2.38 (1 H, m), 2.14 (2 H, m), [1.78–1.42 (5 H, m and 2dq), 1.66, 1.51 (each dq, each ^2J 14.6, ^3J 7.2, CH_2CH_3)] and 0.76 (3 H, J 7.2, CH_3CH_2); δ_C 211.4 (s), 95.6 (s), 84.0 (s), 39.3 (d), 37.7 (t), 33.5 (t), 32.9 (t), 26.6 (t), 22.7 (t) and 5.8 (q); *m/z* 166 (M − HNO_2, 12%), 125 (63), 109 (12), 81 (19) and 57 (100).

The enamine **13** (0.8 g, 2.2 mmol) was allowed to react with an equimolar amount of the nitroolefin **5f** in dry ether at room temp., to give after 3 h a crystalline product which was identified as {1S*-[1R* (or S*), 2R* (or S*)]-3aα, 6aα}-1-*ethyl*-2-*morpholino*-6a-*nitro*-3-(2-*nitrocyclopentyl*)-1,3a,4,5,6,6a-*hexahydropentalen*-1-*ol* **20** (1.30 g, 85%), m.p. 131 °C from ethanol (Found: C, 57.9; H, 7.3; N, 10.55. $C_{19}H_{29}N_3O_6$ requires C, 57.71; H, 7.39; N, 10.63%); ν_{max}/cm^{-1} 3420 (OH), 1640 (C=C), 1550, 1530 (NO_2) and 1100 (COC); δ_H(60 MHz) 4.95 (1 H, m, $CHNO_2$), 4.0 (1 H, m, 3a-H), 3.7 [5 H, m, $(CH_2)_2O$, OH], 2.9 [4 H, m, $(CH_2)_2N$], 2.2–1.8 (15 H, m) and 1.1 (3 H, t, J 7, CH_3CH_2); δ_C 148.5 (s), 136.1 (s), 107.1 (s), 89.1 (d), 85.7 (s), 67.6 (2t), 52.0 (2t), 51.8 (d), 45.5 (d), 34.6 (t), 32.3 (t), 31.1 (t), 30.8 (t), 28.6 (t), 25.8 (t), 23.6 (t) and 7.5 (q); *m/z* 395 (M^+, 36%), 349 (M − NO_2, 78), 298 (44), 245 (48), 125 (72), 105 (40), 91 (47) and 57 (100).

The same reaction carried out on the isomer **14** led to {1R*-[1R* (or S*), 2R* (or S*)]-3aβ, 6aβ}-1-*ethyl*-2-*morpholino*-6a-*nitro*-3-(2-*nitrocyclopentyl*)-1,3a,4,5,6,6a-*hexahydropentalen*-1-*ol* **21** (1.22 g, 80%), m.p. 126 °C from methanol (Found: C, 57.9; H, 7.4; N, 10.5. $C_{19}H_{29}N_3O_6$ requires C, 57.71; H, 7.39; N, 10.63%); ν_{max}/cm^{-1} 3400 (OH), 1640 (C=C), 1540, 1525 (NO_2) and 1100 (COC); δ_H(60 MHz) 5.2 (m, 1 H, $CHNO_2$), 4.0 (1 H, m, 6a-H), 3.7 [4 H, m, $(CH_2)_2O$], 2.9 [4 H, m, $(CH_2)_2N$], 2.3–1.7 (16 H, m) and 0.8 (3 H, t, J 7, CH_3CH_2); δ_C 145.4 (s), 133.3 (s), 106.9 (s), 90.1 (d), 89.1 (s), 67.5 (2t), 52.0 (2t), 50.3 (d), 45.3 (d), 36.7 (t), 32.3 (2t), 31.4 (t), 29.9 (t), 24.3 (t), 23.8 (t) and 8.9 (q); *m/z* 395 (M^+, 36%), 349 (M − NO_2, 78), 298 (44), 245 (48), 125 (72), 91 (47) and 57 (100).

Reaction of **2** *with* 1-*Nitrocyclohexene* **5g**.—The nitroolefin **5g** (0.75 g, 5.9 mmol) was added to the enamine **2** (1 g, 5.9 mmol) at −40 °C; after 24 h at −20 °C dry ether was added and the solid product formed was separated and identified as 4,4a,5,6,7,8-*hexahydro*-3H-3-*morpholino*-3-*propionyl*-2,1-*benzoxazine* N-*oxide* **15** (1.66 g, 95%), m.p. 88 °C (Found: C, 60.6; H, 8.25; N, 9.5. $C_{15}H_{24}N_2O_4$ requires C, 70.79; H, 8.16; N, 9.45%); ν_{max}/cm^{-1} 1720 (C=O), 1600 (C=$\overset{+}{N}$–$\overset{-}{O}$) and 1100 (COC); δ_H(60 MHz) 3.8 [4 H, m, $(CH_2)_2O$], 3.0–2.5 (7 H, m), 2.1–1.8 (10 H, m) and 1.1 (3 H, t, J 7, CH_3CH_2); δ_C 207.7 (s), 123.4 (s), 99.7 (s), 67.0 (2t), 46.2 (2t), 33.1 (d), 33.0 (t), 31.0 (t), 29.2 (t), 27.1 (t), 24.5 (t), 24.4 (t) and 7.5 (q); *m/z* 296 (M^+, 5%), 250 (M − NO_2, 10), 220 (5), 184 (19), 169 (25), 112 (89), 81 (70) and 57 (100). At room temp. in $CDCl_3$ the oxazine **15** was completely converted within 72 h into [1R*-(1α,3aβ,7aβ)-1-*ethyl*-3a,4,5,6,7,7a-*hexahydro*-2-*morpholino*-7a-*nitro*-1H-*inden*-1-*ol* **16**, m.p. 139 °C (Found: C, 60.9; H, 8.05; N, 9.4. $C_{15}H_{24}N_2O_4$ requires C, 60.79; H, 8.16; N, 9.45); ν_{max}/cm^{-1} 3390 (OH), 1620 (C=C), 1525, 1370 (NO_2) and 1105 (COC); δ_H(60 MHz) 4.3 (1 H, d, J 2, C=CH), 3.8 [5 H, m, $(CH_2)_2O$ and 3a-H], 3.4–1.7 (15 H, m) and 1.1 (3 H, t, J 7, CH_3CH_2); δ_C 149.8 (s), 109.5 (s), 104.1 (d), 87.2 (s), 66.8 (2t), 49.2 (2t), 39.0 (d), 31.0 (t), 29.3 (t), 26.4 (t), 21.5 (t), 21.0 (t) and 8.1 (q); *m/z* 296 (M^+, 24%), 250 (M − NO_2, 100), 249 (M − HNO_2, 68), 220 (79), 184 (29) and 57 (100).

Hydrolysis of the enamine **16** (0.65 g, 2.2 mmol) carried out at pH 2 in methanol and HCl (10%) afforded the corresponding ketone, identified as [1R*-(1α,3aβ,7aβ)-1-*ethyl*-1-*hydroxy*-7a-*nitrooctahydroinden*-2-*one* **19** (0.45 g, 90%), m.p. 128 °C from methanol (Found: C, 58.3; H, 7.4; N, 6.3. $C_{11}H_{17}NO_4$ requires C, 58.14; H, 7.54; N, 6.30); ν_{max}/cm^{-1} 3590 (OH), 1750 (C=O), 1540 and 1365 (NO_2); δ_H(300 MHz) 3.39 (1 H, m, $w_{H/2}$ 24.0, 3a-H), 2.86 (1 H, br s, OH), 2.71 (1 H, br d), 2.64, 2.24 (2 H, dq, part AB of an ABX system, J_{AB} 20.1, J_{AX} 11.0, J_{BX} 10.8 CH_2CO), 1.86 (1 H, tt, J_1 4.7, J_2 14.1), 1.74, 1.37 (each 1 H, each dq, each ^2J 14.1 and ^3J 7.0, CH_2CH_3), 1.60 (3 H, m), 1.23 (2 H, m), 1.15 (1 H, m) and 0.79 (3 H, t, J 7, CH_3CH_2); δ_C 210.5 (s), 94.6 (s), 85.6 (s), 36.3 (t), 31.6 (d), 28.6 (t), 25.2 (t), 23.9 (t), 20.9 (t), 19.1 (t) and 6.6 (q); *m/z* 227 (M^+, 1%), 210 (M^+ − OH, 12), 209 (M − H_2O, 8), 181 (M − NO_2, 4), 180 (M^+ − HNO_2, 11), 149 (41), 95 (11), 82 (14) and 57 (100).

Reaction of **3** *with* 1-*Nitropropene* **5a**.—The nitroolefin **5a** (0.48 g, 5.5 mmol) was added to the enamine **3** (1.0 g, 5.5 mmol) at −20 °C; after 24 h at −18 °C, 1-*ethyl*-3,4-*dimethyl*-2-*morpholino*-5-*nitrocyclopent*-2-*enol* **23a** was detected as a crude product by the following signals: ν_{max}/cm^{-1} 3400 (OH), 1650 (C=C), 1540 and 1370 (NO_2); δ_H 5.0 (d, J 7, $CHNO_2$), 1.75 (s, 3-Me), 1.1 (d, J 6.5, 4-Me) and 0.85 (t, J 7, CH_3CH_2).

The crude product was dissolved in $CHCl_3$ (10 cm^3), after which the solution was diluted with water and acidified to pH 5 with 10% HCl; after being stirred vigorously for 24 h the organic layer was separated, washed with sat. aq. $NaHCO_3$ and water and dried (Na_2SO_4); flash chromatography of the oily residue using benzene–acetone (9:1) as eluent, afforded a crystalline product which was identified as 2-*ethyl*-2-*hydroxy*-4,5-*dimethyl*-3-*nitrocyclopentanone* **24a** (0.77 g, 70% yield), m.p. 78 °C (from chloroform–hexane) (Found: C, 53.8; H, 7.5; N, 6.9. $C_9H_{15}NO_4$ requires C, 53.72; H, 7.51; N, 6.96%); ν_{max}/cm^{-1} 3450 (OH), 1740 (C=O), 1540 and 1360 (NO_2); δ_H(200 MHz) 4.92 (1 H, d, J 5.3, $CHNO_2$), 2.95 (1 H, br s, OH), 2.44, 2.38 (1 H, dq, $^3J'$ 7.5, $^3J''$ 11.2, 5-H), 2.15 (1 H, m, 4-H), 1.68, 1.56 (each 1 H, each dq, each ^2J 14.9 and ^3J 7.2, CH_2CH_3), 1.22 (3 H, d, J 7.5, 5-Me), 1.18 (3 H, d, J 6.7, 4-Me) and 0.98 (3 H, t, J 7.2, CH_3CH_2); *m/z* 201 (M^+, 0.1%), 183 (M − H_2O, 2), 154 (M − HNO_2, 7), 99 (76), 81 (17), 69 (26) and 57 (100).

Reaction of **3** *with* 2-*Nitropropene* **5b**.—The nitroalkene **5b** (0.48 g, 5.5 mmol) was added at −20 °C to the α-ketoenamine **3** (1.0 g, 5.5 mmol); after 2 h at −20 °C the compound 5,6-dihydro-3,5-dimethyl-6-morpholino-6-propionyl-4H-1,2-oxazine *N*-oxide **22** could be detected by IR spectroscopy; ν_{max}/cm^{-1} 1705 (C=O), 1620 (C=$\overset{+}{N}$–$\overset{-}{O}$) and 1105 (COC). After 5 min at room temp. the oily crude product was treated with dry ether to give separation of 1-*ethyl*-3,5-*dimethyl*-2-*morpholino*-5-*nitrocyclopent*-2-*enol* **23b** (1.43 g, 96% yield), m.p. 97 °C (Found: C, 57.9; H, 8.15; N, 10.3. $C_{13}H_{22}N_2O_4$ requires C, 57.76; H, 8.20; N, 10.36%); ν_{max}/cm^{-1} 3430 (OH), 1660 (C=C), 1530, 1380 (NO_2) and 1105 (COC); δ_H(60 MHz) 3.7 [4 H, m, $(CH_2)_2O$], 3.2 [4 H, m, $(CH_2)_2N$], 2.6–2.0 (3 H, m and br s, 4-H and OH), 1.9 (3 H, s, 5-Me), 1.7 (3 H, s, 3-Me), 1.6 (2 H, q, J 7, CH_2CH_3) and 1.0 (3 H, t, J 7, CH_3CH_2); δ_C 143.8 (s), 127.4 (s), 97.0 (s), 86.9 (s), 68.3 (t), 51.8 (t), 46.2 (t), 29.4 (t), 21.6 (q), 15.1 (q) and 8.9 (q); *m/z* 270 (M^+, 18%), 253 (M − OH, 2), 224 (M − NO_2, 33), 221 (33), 196 (41), 180 (26), 167 (30), 150 (20), 142 (18), 136 (25), 126 (29), 114 (38), 98 (31), 86 (40), 70 (42) 57 (86) and 41 (100).

The product **23b** was hydrolysed under the conditions

described above to yield the corresponding ketone *2-ethyl-2-hydroxy-3,5-dimethyl-3-nitrocyclopentanone* as an inseparable mixture of diastereoisomers **24b**, **24'b** (ratio approximately 2:1, by ^{1}H NMR spectroscopy), m.p. of the mixture 120–121 °C (Found: C, 53.7; H, 7.6; N, 6.85. $C_9H_{15}NO_4$ requires C, 53.72; H, 7.51; N, 6.96%); ν_{max}/cm^{-1} 3450 (OH), 1755 (C=O), 1540, 1370 and 1350 (NO_2); δ_H(200 MHz) 3.05 (1 H, br s, OH), 2.92–2.40 (3 H, m, 5-H and 4-H), 1.77, 1.47 (each 1 H, each dq, each ^2J 14.8 and ^3J 7.1, CH_2CH_3), 1.69, 1.67 (3 H, each s, rel. int. 1:2, 3-Me), 1.32, 1.22 (3 H, each d, rel. int. 2:1, J 6.7 and 7.4 respectively, 5-Me), 0.87 and 0.84 (3 H, each t, rel. int. 1:2, each J 7.1, CH_3CH_2); δ_C 215.7, 214.6 (each s), 95.2, 93.9 (each s), 83.9, 83.3 (each s), 39.7, 39.5 (each d), 37.7, 36.3 (each t), 27.8, 27.0 (each t), 17.8, 17.6, 17.4 (each q), 15.7 (q) and 6.8 (2q); m/z 155 (M − NO_2, 1%), 123 (25), 113 (14), 99 (25), 74 (10), 69 (33) and 57 (100).

Reaction of **3** *with* β-*Nitrostyrene* **5c**.—The nitroalkene **5c** (0.81 g, 5.5 mmol) was added in one portion to the α-ketoenamine **3** (1.0 g, 5.5 mmol) at room temp. and the mixture was left at 5 °C for 24 h; after this time compound **23c** 1-ethyl-3-methyl-2-morpholino-5-nitro-4-phenylcyclopent-2-enol was detected in the reaction mixture by the following signals: ν_{max}/cm^{-1} 3420 (OH), 1660 (C=C), 1535, 1370 (NO_2) and 1110 (COC); δ_H 4.9 (d, J 9, $CHNO_2$), 1.6 (s, 3-Me) and 0.9 (t, J 7, CH_3CH_2).

The crude product was hydrolysed using the procedure described above and from the oily residue a crystalline product was separated by treatment with hexane; it was identified as *2-ethyl-2-hydroxy-5-methyl-3-nitro-4-phenylcyclopentanone* **24c**, m.p. 180–181 °C from chloroform–hexane (Found: C, 63.95; H, 6.45; N, 5.25. $C_{14}H_{17}NO_4$ requires C, 63.87; H, 6.51; N, 5.32); ν_{max}/cm^{-1} 3470 (OH), 1755 (C=O), 1545 and 1370 (NO_2); δ_H(C_6D_6; 60 MHz) 7.2 (5 H, m, Ph), 5.1 (1 H, d, J 11), 3.4 (1 H, dd, J_1 12.5, J_2 11, CHPh), 2.7 (1 H, br s, OH), 2.2 (1 H, m, 5-H), 1.5 (2 H, q, J 7, CH_2CH_3), 0.9 (3 H, d, J 7, 5-Me) and 0.8 (3 H, t, J 7, CH_3CH_2); m/z 245 (M − H_2O, 28%), 216 (M − HNO_2, 27), 199 (M − NO_2, 15), 161 (60), 143 (40), 128 (46), 115 (45), 105 (24), 91 (54), 77 (50) and 57 (100).

Reaction of **3** *with* 2-*nitro*-1-*phenylpropene* **5d**.—The nitroalkene **5d** (0.90 g, 5.5 mmol) was added to the α-ketoenamine **3** (1.0 g, 5.5 mmol) at 0°C, and the mixture left at 5°C; after 24 h compound **23d** 1-ethyl-3,5-dimethyl-2-morpholino-5-nitro-4-phenylcyclopent-2-enol was detected by the following signals: ν_{max}/cm^{-1} 3480 (OH), 1660 (C=C), 1530, 1360 (NO_2) and 1105 (COC); δ_H 1.9 (s, 5-Me), 1.7 (s, 3-Me) and 1.0 (t, J 7, CH_3CH_2). The crude product was hydrolysed using the procedure described above; flash chromatography of the oily residue using ethyl acetate–light petroleum (1:9) as eluent afforded compound **24d**, m.p. 156–157°C from chloroform–hexane (Found: C, 64.9; H, 6.95; N, 5.0. $C_{15}H_{19}NO_4$ requires C, 64.97; H, 6.91; N, 5.05%); ν_{max}/cm^{-1} 3460 (OH), 1760 (C=O), 1540 and 1370 (NO_2); δ_H (200 MHz) 7.35 (3 H, m, *m*- and *p*-ArH), 7.13 (2 H, m, *o*-ArH), 3.22–3.12 (3 H, m, OH, 3-H, CHPh), 1.90, 1.65 (each 1 H, each dq, each ^2J 14.5 and ^3J 7.2, CH_2CH_3), 1.52 (3 H, s, 3-Me), 1.22 (3 H, d, J 6.4, 5-Me), and 0.96 (3 H, t, J 7.2, CH_3CH_2); m/z 230 (M − HNO_2, 14%), 199 (26), 145 (100), 117 (95), 115 (81), 91 (61), 77 (45) and 57 (60).

Reaction of **3** *with* 1-*Nitrocyclopentene* **5f**.—The nitroolefin **5f** (0.62 g, 5.5 mmol) was added at 0 °C to the α-ketoenamine **3** (1.0 g, 5.5 mmol); after 3 h at room temp. treatment of the crude product with hexane–ether allowed the isolation and identification of 3,4,4a,5,6,7-*hexahydro*-4-*methyl*-3-*morpholino*-3-*propionylcyclopent*[c][1,2]*oxazine* N-*oxide* **25** (1.40 g, 86%), m.p. 90–92 °C (Found: C, 60.9; H, 8.1; N, 9.55. $C_{15}H_{24}N_2O_4$ requires C, 60.79; H, 8.16; N, 9.45%); ν_{max}/cm^{-1} 1720 (C=O), 1650 (C=$\overset{+}{N}$–$\overset{-}{O}$) and 1105 (COC); δ_H(60 MHz) 3.7 [4 H, m, $(CH_2)_2O$], 3.1–2.5 (8 H, m), 2.1–1.7 (6 H, m), 1.3 (3 H, d, J 6.7, 4-Me), 1.0 (3 H, J 7.0, CH_3CH_2); m/z 296 (M$^+$, 21%), 250 (M − NO_2, 21), 221 (14), 192 (14), 183 (16), 163 (14), 126 (100), 114 (48), 110 (41), 91 (12), 86 (55), 70 (28) and 57 (88). In $CDCl_3$ the oxazine derivative was transformed into an inseparable 50% mixture of compounds **26** and **27**, which was attributed the structure of [1S*-(1α,3aα,6aα)]- and [1R*-(1α,3aβ,6aβ)]-1-*ethyl*-3-*methyl*-2-*morpholino*-6a-*nitro*-1,3a,4,5,6,6a-*hexahydropentalen*-1-*ol*, m.p. of the mixture 89 °C (Found: 3, 60.65; H, 8.15; N, 9.5. $C_{15}H_{24}N_2O_4$ requires C, 60.79; H, 8.16; N, 9.45%); ν_{max}/cm^{-1} 3480, 3320 (OH), 1540, 1530, 1370, 1360 (NO_2), 1110 and 1105 (COC); δ_H(200 MHz) 3.93–3.65 [5 H, m, $(CH_2)_2O$, 3a-H], 3.12–2.90 [4 H, m, $(CH_2)_2N$], 2.61 (1 H, m), [2.18–1.42 (11 H, m and s), 1.72 (s, 3-Me)], 1.08 and 0.75 (3 H, each t, rel. int. 1:1, each J 7, CH_3CH_2); m/z 296 (M$^+$, 22%), 250 (M − NO_2, 20), 221 (15), 205 (10), 192 (10), 163 (13), 136 (18), 125 (29), 114 (22), 95 (22), 86 (25), 70 (18), 67 (31) and 57 (100).

The mixture was hydrolysed under the conditions described above to give the corresponding ketone as a pair of diastereoisomers **28** and **29** in ratio *ca.* 1:1 (by ^{1}H NMR spectroscopy), identified as [1R*-(3S*,1α,3aα,6aα)- *and* [1R*-(3S*,1α,3aβ,6aβ)]-1-*ethyl*-1-*hydroxy*-3-*methyl*-6a-*nitrohexahydropentalen*-2-*one*, m.p. of the mixture 73 °C; ν_{max}/cm^{-1} 3480, 3460 (OH), 1750br (C=O), 1540, 1530, 1375 and 1370 (NO_2); δ_H 3.05, 2.90 (2 H, each m, **29**- and **28**-3a-H, **28**- and **29**-OH), 2.68 (0.5 H, q, J 8.3), 2.52 (0.5 H, m), [2.38–1.95 (4 H, m and 2 q), 2.32, 2.05 (each q, J 6.7 and 7.4 respectively, **28**- and **29**-3-H)], [1.87–1.40 (4 H, m and 4 dq), 1.79, 1.45 (each dq, ^2J 14.1 and ^3J 7.4, **28**-CH_2CH_3), 1.62, 1.55 (each dq, each ^2J 15.1 and ^3J 7.5, **29**-CH_2CH_3)], 1.30, 1.29 (3 H, each d, rel. int. 1:1, J 6.7 and 7.4 respectively, **28**- and **29**-3-Me), 0.87 and 0.83 (3 H, each t, rel. int. 1:1, J 7.4 and 7.5 respectively, **28**- and **29**-CH_3CH_2). Recrystallization from hexane allowed the separation of the pure isomer **28**, m.p. 117 °C (Found: C, 58.05; H, 7.65; N, 6.1. $C_{11}H_{17}NO_4$ requires C, 58.14; H, 7.54; N, 6.16%); ν_{max}/cm^{-1} 3460 (OH), 1745 (C=O), 1530 and 1375 (NO_2); δ_H 3.08 (1 H, s, OH), 2.90 (1 H, m, 3a-H), 2.68 (1 H, q, J 8.3), 2.36 (1 H, m), 2.32 (1 H, q, J 6.7, 3-H), 2.21–1.91 (4 H, m), 1.79, 1.45 (each 1 H, each dq, each ^2J 14.1 and ^3J 7.4, CH_2CH_3), 1.30 (3 H, d, J 6.7, 3-Me) and 0.87 (3 H, t, J 7.4, CH_3CH_2); m/z 227 (M$^+$, 0.5%), 210 (M − OH, 3), 209 (M − H_2O, 2), 181 (M − NO_2, 17), 180 (M − HNO_2, 34), 125 (17), 105 (32), 99 (56) and 57 (100).

Reaction of **4** *with* 1-*Nitropropene* **5a**.—The nitroolefin **5a** (0.30 g, 3.4 mmol) was added to the α-ketoenamine **4** (1.0 g, 3.4 mmol) at 0 °C; after 12 h dry ether was added to the mixture to give a solid which was filtered off, washed with ether and identified as 4-*methyl*-2-*morpholino*-5-*nitro*-1,3-*diphenylcyclopent*-2-*enol* **30a** (1.10 g, 85%), m.p. 156–157 °C (Found: C, 69.6; H, 6.2; N, 7.4. $C_{22}H_{24}N_2O_4$ requires C, 69.46; H, 6.36; N, 7.36); ν_{max}/cm^{-1} 3350 (OH), 1640 (C=C), 1540, 1370 (NO_2) and 1090 (COC); δ_H(60 MHz) 7.4 (10 H, m, 2 Ph), 4.7 (1 H, d, J 3, $CHNO_2$), 3.8 (1 H, m, 4-H), 3.4 [5 H, m, $(CH_2)_2O$, OH], 2.6 [4 H, m, $(CH_2)_2N$] and 1.0 (3 H, d, J 7, 4-Me); δ_C 145.1 (s), 137.9 (s), 136.7 (s), 129.9 (d), 129.3 (d), 128.7 (d), 128.0 (d), 125.9 (d), 123.6 (s), 99.8 (d), 83.6 (s), 67.5 (2t), 50.7 (2t), 43.8 (d) and 18.7 (q); m/z 380 (M$^+$, 35%), 334 (M − NO_2, 30), 316 (100), 257 (52), 242 (39), 129 (39), 116 (84), 105 (89), 97 (47), 87 (27), 77 (93) and 41 (72).

Reaction of **4** *with* 2-*Nitropropene* **5b**.—The nitrolefin **5b** (0.30 g, 3.4 mmol) was added to the α-ketoenamine **4** (1.0 g, 3.4 mmol) at 0 °C; after 2 h the solid which had formed was separated with the aid of a small amount of dry ether and identified as 5-*methyl*-2-*morpholino*-5-*nitro*-1,3-*diphenylcyclopent*-2-*enol* **30b** (1.18 g, 92%), m.p. 161 °C (Found: C, 69.5; H, 6.3; N, 7.45. $C_{22}H_{24}N_2O_4$ requires C, 69.46; H, 6.36; N, 7.36); ν_{max}/cm^{-1} 3350 (OH), 1640

(C=C), 1520, 1370 (NO_2) and 1100 (COC); δ_H(60 MHz) 7.4 (10 H, m, 2 Ph), 4.3 (1 H, br s, OH), 3.9, 2.9 (2 H, dd, J_{gem} 16, 3-H), 3.5 [4 H, m, $(CH_2)_2O$], 2.6 [4 H, m, $(CH_2)_2N$] and 2.0 (3 H, s, 5-Me); δ_C 143.8 (s), 138.5 (s), 135.2 (s), 127.7 (d), 127.3 (d), 126.8 (d), 124.9 (d), 124.6 (d), 121.0 (s), 95.4 (s), 82.9 (s), 66.1 (2t), 49.2 (2t), 41.9 (t) and 23.6 (q); *m/z* 380 (M^+, 4%), 334 (M − NO_2, 3%), 306 (6), 188 (12), 105 (100), 87 (86) and 77 (54).

Reaction of **4** *with* β-*Nitrostyrene* **5c**.—The nitroalkene **5c** (0.61 g, 4.0 mmol) was added to the α-ketoenamine **4** (1.2 g, 4.0 mmol) at room temp.; after 24 h dry ether was added to the mixture to give a crystalline product which was identified as 2-*morpholino*-5-*nitro*-1,3,4-*triphenylcyclopent*-2-*enol* **30c** (1.70 g, 96%), m.p. 188 °C (Found: C, 73.4; H, 5.2; N, 6.45. $C_{27}H_{26}N_2O_4$ requires C, 73.29; H, 5.29; N, 6.33%); ν_{max}/cm^{-1} 3420 (OH), 1600 (C=C), 1540, 1370 (NO_2) and 1100 (COC); $\delta_H(C_6D_6$; 60 MHz) 7.8–7.2 (15 H, m, 3 Ph), 5.3, 5.2 (2 H, dd, J_{AB} 6, $CHNO_2$ and C*H*Ph), 3.1 [5 H, m, $(CH_2)_2O$ and OH], and 2.7 [4 H, m, $(CH_2)_2N$]; δ_C 143.1 (s), 137.4 (s), 133.4 (s), 130.6 (s), 128.5 (d), 127.9 (d), 127.8 (d), 127.3 (d), 126.5 (d), 126.4 (d), 126.3 (d), 124.6 (d), 118.0 (s), 99.7 (d), 82.9 (s), 66.0 (2t), 52.4 (d) and 49.4 (2t); *m/z* 442 (M^+, 2%), 396 (M − NO_2, 1), 178 (13), 165 (3), 152 (74), 149 (5), 114 (10), 105 (100), 91 (11) and 77 (85).

Reaction of **4** with 1-*nitrocyclopentene* **5f**.—The nitroolefin **5f** (0.45 g, 4.0 mmol) was added to the α-ketoenamine **4** (1.2 g, 4.0 mmol) at 0 °C; after 12 h, treatment of the mixture with dry ether gave a solid which was identified as 5-*morpholino*-3a-*nitro*-4,6-*diphenyl*-1,2,3,3a,4,6a-*hexahydropentalen*-4-*ol* **30f**. (1.56 g, 96%), m.p. 197 °C (Found: C, 70.85; H, 6.5; N, 6.8. $C_{24}H_{26}N_2O_4$ requires C, 70.92; H, 6.45; N, 6.89%); ν_{max}/cm^{-1} 3350 (OH), 1640 (C=C), 1530, 1370 (NO_2) and 1100 (COC); δ_H(60 MHz) 7.4 (10 H, m, 2 Ph), 4.4 (1 H, m, 6a-H), 3.3 [4 H, m, $(CH_2)_2O$], 3.1 (1 H, br s, OH), 2.7 [4 H, m, $(CH_2)_2N$] and 1.9–1.7 [6 H, m, $(CH_2)_3$]; δ_C 143.3 (s), 141.0 (s), 137.0 (s), 129.4 (d), 128.3 (d), 128.2 (d), 127.2 (d), 120.3 (s), 107.2 (s), 85.9 (s), 67.0 (2t), 54.6 (d), 50.3 (2t), 36.1 (t), 30.4 (t) and 25.7 (t); *m/z* 406 (M^+, 21%), 360 (M − NO_2, 26), 293 (25), 273 (24), 188 (48), 105 (86), 91 (46), 87 (100) and 77 (81).

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