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1-SUBSTITUTED MORPHOLINO ETHENES–III[1]

CARBOCYCLIC AND ALIPHATIC HETEROCYCLIC COMPOUNDS FROM 5-MEMBERED RING DERIVATIVES

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Abstract—[4+2] Cycloaddition reaction of 1-(cyclopenten-1-yl)-1-morpholino ethene with β-nitrostyrene leads to tetrahydroindan and tetrahydroindanone derivatives. A [4+2] adduct of interest is also obtained in the reaction of the same substrate with mesyl chloride. Reactivity of the same electrophiles with the morpholino enamine of cyclopentyl-methyl ketone is also examined. Some stereochemical aspects of the above mentioned reactions are discussed.

The previous paper in this series[1,2] discussed the chemical reactivity of 1-substituted-1-morpholino ethenes in which the substituent was a 6-membered ring. The present work deals with analogous substrates in which the substituent is a 5-membered ring, namely compounds **1** and **2** (Schemes 1 and 2). Compound **1** is an equilibrium mixture[3]† of the more and less substituted enamines **a** and **b**. In the reaction with β-nitrostyrene (βNS) in fact, only the nitroalkylated enamine **3**, derived from the isomer **b**, formed in quantitative yield, although in the parent mixture the ratio **a**:**b** was 9:1.

When **1a**⇌**1b** were allowed to react with sulphene, generated *in situ* from mesyl chloride and triethylamine (Scheme 1), the major product was **5**, 3-methyl-3-morpholino-spiro[3,4]-1-thiooctane 1,1-dioxide, as indicated by the presence of a methyl signal at 1.45 δ and of a signal at 3.65 δ of area 2, relative to the methylene of the four-membered ring. The remaining product consisted of a mixture of **6** and **7**. Compound **6** was separated and identified as 3-cyclopentyl-3-morpholino-thietane1,1-dioxide, whereas **7** could not be isolated. However, the presence of **7** was confirmed by isolation of the corresponding ketone **9**, derived from mild acidic hydrolysis of the crude reaction mixture. Ketone **9** could not be derived from **6**, since opening of **6** occurred only on prolonged heating in acidic medium. The same opening reaction did not take place with **5**, even under forcing conditions, in basic or acidic medium. The great stability of **5** was further reflected in the fact that it did not revert into the starting materials, unlike analogous thietane 1,1-dioxides, including **6**.[1]

It is interesting to note that the sulphene, unlike β-nitrostyrene, reacted with the tetrasubstituted isomer **1a**, in spite of its greater steric hindrance than that of **1b**. This seems to be a consequence of the well known high reactivity of this electrophile.

A very interesting behaviour of **2** was found in the reaction with β-nitrostyrene, especially in comparison with the analogous 6-membered ring derivative.[2] It is also of interest that the reaction is solvent-dependent. In fact, when the reaction was carried out in dry ether or *n*-hexane, **10**, **11**, **12** and **13** were obtained in the ratio 7:1:1:1 respectively (Scheme 2). However, when the reaction was performed in absolute ethanol, **10**, **11**, **13** and **14** formed in the ratio 3:6:0.5:0.5. The total yield in both cases was about 85%.

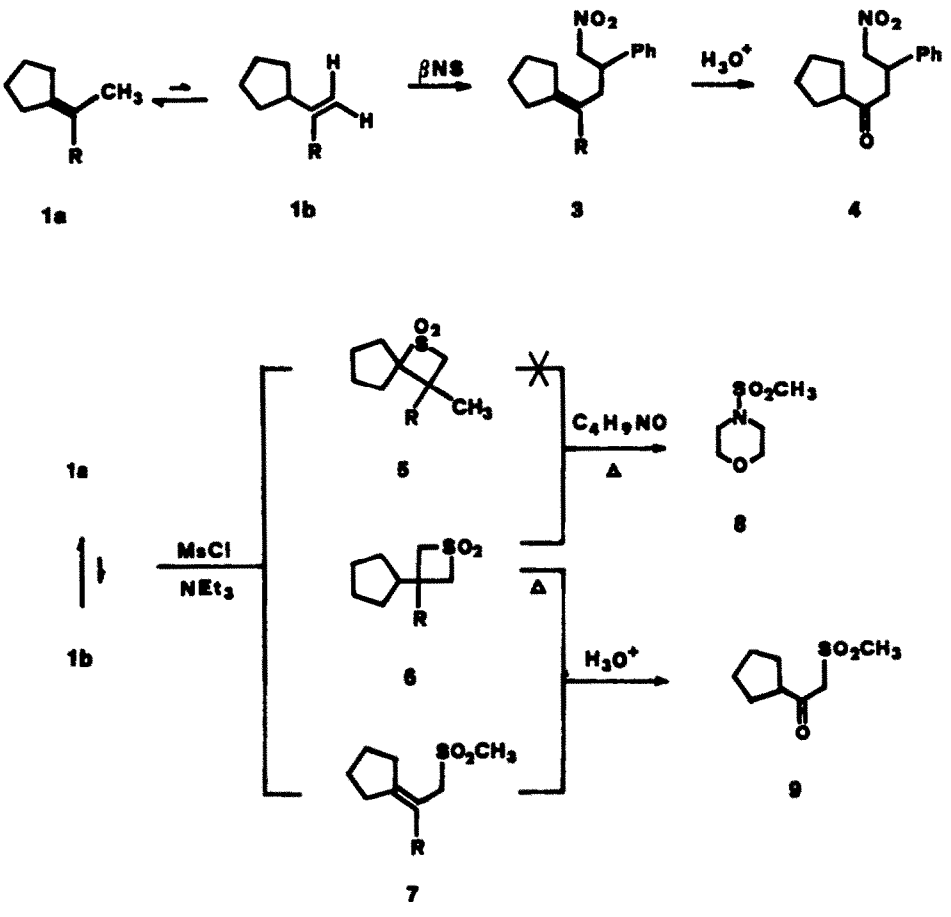
The spectroscopic analyses were consistent with the proposed structure **10**, 2,3,3a,6,7,7a - hexahydro - 4 - morpholino - 7 - nitro - 6 - phenyl - (3aα, 6α, 7β, 7aα) - 1H - indene. The less substituted enamine double bond was confirmed by the IR spectrum (1620 cm^{-1}) and by the ^1H NMR spectrum, in which the vinylic proton signal appeared as a doublet at 4.40 δ, $J_{45} \simeq 2.0$ Hz. The signal of H-7 appeared as a doublet of doublets at 4.8 δ with coupling constants of 10.5 and 3.5 Hz. The benzylic proton signal at 4.0 δ showed long-range couplings, which is consistent with the *quasi*-axial orientation of the C-1 methylene group. Acidic hydrolysis (pH ≃ 6) of **10** afforded the ketone **15** which was assigned the structure of 7 - nitro - 6 - phenyl - (3aα,6α,7β,7aα) - octahydro - 4H - inden - 4 - one, on the basis of the analysis of its ABMX spin system (Fig. 1).

That the fusion between the rings was *cis* was further supported by the fact that **15** did not undergo equilibration in acidic medium under reflux. This is in good agreement with the equilibration results found for the simple hexahydro-hydrindan-4-one system, whose *cis* isomer is more stable than the *trans* one (78:22).[4] Furthermore, in this case the *trans*-fused stereoisomer would have been even less stable, owing to the presence of the two bulky groups (nitro and phenyl) in axial conformation. This readily accounts for the non-equilibration of **15**. Since the conditions used in the hydrolysis were under kinetic control,[2] the same configurational feature as in **15** was assigned to **10**.

Enamine **11**, which was the main product in ethanol, showed the enamine absorption band at 1620 cm^{-1}. The structural assignments for **11** followed from its corresponding ketone **16**, as the NMR spectrum of **11** could not be analyzed. No chiral centre was involved in the hydrolysis of **11** and since this was performed at pH 6–7, no epimerization occurred. Compound **16** was identified as 7 - nitro - 6 - phenyl - (3aβ,6α,7β,7aβ) - octahydro - 4H - inden - 4 - one on the basis of NMR analysis (Fig. 1).

At this point however, nothing could be said about the

†A similar equilibrium could not be evidentiated in the analogous 6-membered ring derivative,[1] at least by chemical methods and under the reaction conditions used.



Scheme 1.

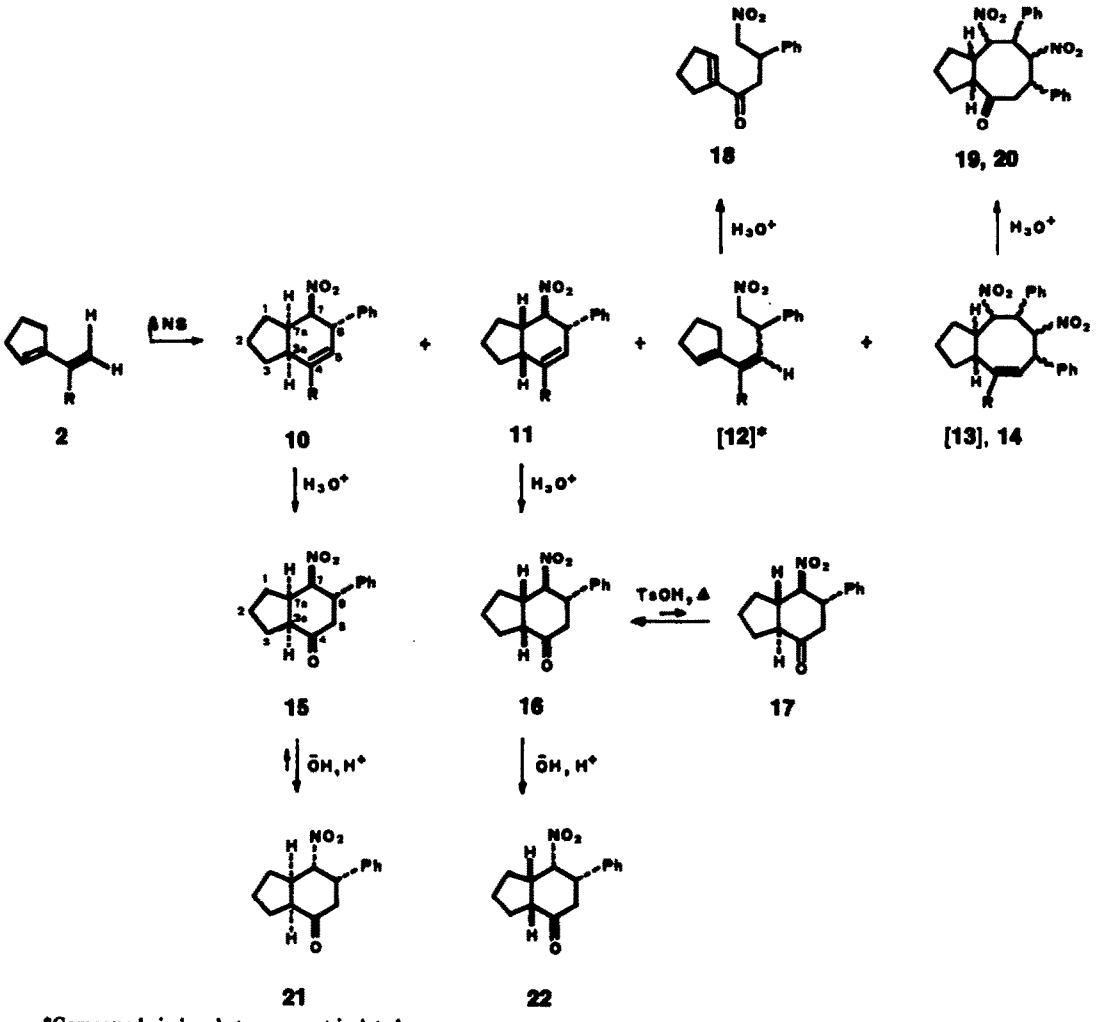
ring junction in **16**, as it could be either *trans* or *cis*. Equilibration of **16** in acidic medium under reflux proceeded to only 20%. The new stereoisomer **17** (Scheme 2) was assigned the structure of 7 - nitro - 6 - phenyl - (3aα,6α,7β,7aβ) - octahydro - 4H - inden - 4 - one, on the basis of NMR analysis (Fig. 1). The coupling constants of the spin -system remained practically unchanged, compared to those of **16**, thus indicating that configurational inversion had occurred only at C-3a. The ratio 80:20 in favour of **16** induced us to think that **16** is the *cis*-fused isomer and **17** the *trans*-fused one.[4]

When the reaction between **2** and β-nitrostyrene was performed in ether, a small amount of ketone **10** was isolated and characterized by spectroscopic methods. Its presence is indicative of the formation of the open-chain enamine **12** and hence of the two-step mechanism, through a zwitterionic intermediate. On the other hand, isolation of a [6.3.0]bicycloundecan-4-one system, both in ether and in ethanol gave further support to this thesis.[5,6] Compounds **13** and **14**, in fact, derived from the attack of a second molecule of the nitroolefin on the intermediate, followed by cyclization.† The stereochemistry of **13** and **14**, as well as their hydrolysis derivatives **19** and **20** respectively is not yet known. However **19** and **20** remained unchanged by acidic treatment under reflux. Evidently they differ in the configuration around the asymmetric centres bearing the substituents of the cyclooctane ring.

Interesting also is the treatment of ketones **15** and **16** with base (Scheme 2). When **15** was treated with sodium hydroxide in absolute ethanol, a 9:1 mixture of **21** and **15** itself was obtained, after addition of acetic acid (pH 6–7). Compound **21** was identified as 7 - nitro - 6 - phenyl - (3aα,6α,7α,7aα) - octahydro - 4H - inden - 4 - one. Its NMR spectrum showed the nitromethinic proton signal at 4.5 δ as a doublet of doublets, with coupling constants of 3.5 and 3.0 Hz, which are consistent with the equatorial orientation of the phenyl group and axial orientation of the nitro group. The signal of the benzylic proton in fact had $W_H = 13.5$ Hz. The mechanism of this epimerization involved formation of the nitronate salt (243 nm, ϵ_{max}^{EtOH} 8200) which gave the corresponding nitronic acid (230 nm, ϵ_{max}^{EtOH} 8200) by acidification with hydrochloric acid.[2] Acidification of the solution containing the nitronate salt with acetic acid led to **21** by a highly stereoselective attack on the proton from the less hindered side of the molecule (β).[9]

When the ketone **16** underwent an analogous treatment, the corresponding nitronate salt was obtained first (242 nm, ϵ_{max}^{EtOH} 3700), which gave the nitronic acid (236 nm, ϵ_{max}^{EtOH} 4500) under similar conditions as above. By standing or by adding acetic acid, the nitronate salt yielded the ketone **22** exclusively and quantitatively, by a stereospecific β attack of the proton. In both cases the

†A few cases are reported in the literature[7,8] in which 1 mole of enamine reacted with 2 moles of the nitroolefin. The resulting cyclic products however always contained a 6-membered ring.



*Compounds in brackets were not isolated
R = morpholino–

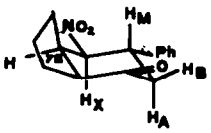
Scheme 2.

protonation of the nitronate salts took place in a way similar to the monocyclic nitronate salts[9] and different from the decalone derivatives.[2] The new ketone 22 was assigned the structure of 7 - nitro - 6 - phenyl - (3aβ,6α,7α,7aβ) - octahydro - 4H - inden - 4 - one. The nitromethinic proton signal appeared at 5.0 δ as a narrow doublet of doublets with coupling constants of 3.0 and 5.5 Hz. The benzylic proton signal appeared as a broad peak centred at 3.6 δ, $W_H \simeq 13.5$ Hz, partially concealed beneath other signals.

As to the mechanism of the reaction between 2 and β-nitrostyrene, it is evident from these results that a change in solvent from non-polar to polar also favours a two-step mechanism.[5] Ethanol in fact would so stabilize the dipolar intermediate as to allow conformational rotations to occur (Scheme 3). The β attack of the carbon anion onto the electrophilic centre would lead to the tetrasubstituted enamine 23 and consequently to 10.

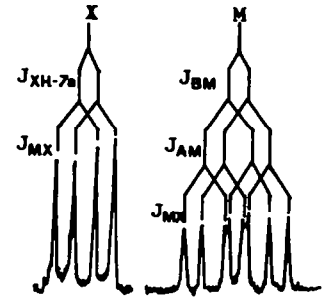
Similarly the α attack would furnish enamine 24 and consequently 11. The less substituted enamines 10 and 11 proved thermodynamically more stable than their respective more substituted counterparts 23 and 24. In fact the latter were not isolated. However, a reaction carried out in NMR tube showed that they formed first but they isomerized in a few minutes to give 10 and 11 respectively. The driving force of this equilibration seems to be the strains suffered by the two rings, together with a severe $A^{(1,3)}$ strain[10] between the morpholine ring and the near methylene group of the 5-membered ring. However, similar more substituted tetrahydroindan derivatives, obtained from 1-vinyl-cyclopentene and *trans*-β-methyl-β-nitrostyrene by Diels–Alder reaction,[11] proved very stable. It seems evident that in the present case the base plays an important role in the stability of this type of double bonds, probably through electronic factors.

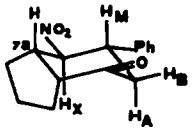
As with dienamines,[12] for the cross-conjugated enamine 2 the [4+2]cycloaddition of sulphene was found to be competitive with the [2+2]cycloaddition, as 26 formed together with 25 in ratio 3:4 (Scheme 4). The thietane 1,1-dioxide 25 was characterized at the presence of a peak at 4.25 δ of area 4, relative to the methylene groups of the four-membered ring. Basic treatment of 25 in ethanol under reflux led to the open-chain enamine 27, which showed two vinylic proton signals at 5.0 and 5.9 δ. The presence of two carbon–carbon double bonds was also indicated by two IR band at 1630 and 1560 cm^{-1}. Hydrolysis of 27, carried out in acidic medium, gave the corresponding ketone 28, in contrast to what was found in the case of the analogous six-membered ring derivative.[1]



15

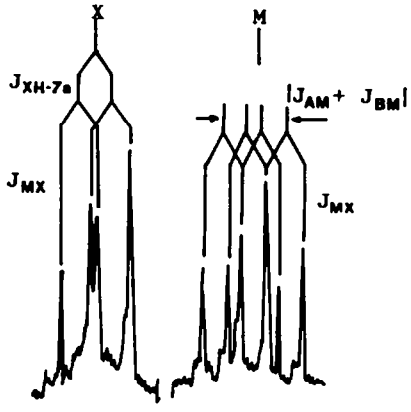
$|J_{AB}| = 14.2$ Hz
$J_{AM} = 12.7$ Hz
$J_{BM} = 5.2$ Hz
$J_{MX} = 11.7$ Hz
$J_{XH\text{-}7a} = 5.0$ Hz

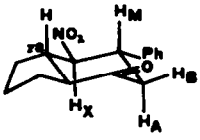




16

$|J_{AM} + J_{BM}| = 18.7$ Hz
$J_{MX} = 11.2$ Hz
$J_{XH\text{-}7a} = 10.3$ Hz





17

$|J_{AM} + J_{BM}| = 18.7$ Hz
$J_{MX} = 10.5$ Hz
$J_{XH\text{-}7a} = 9.7$ Hz

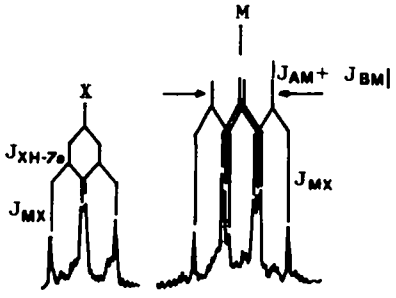


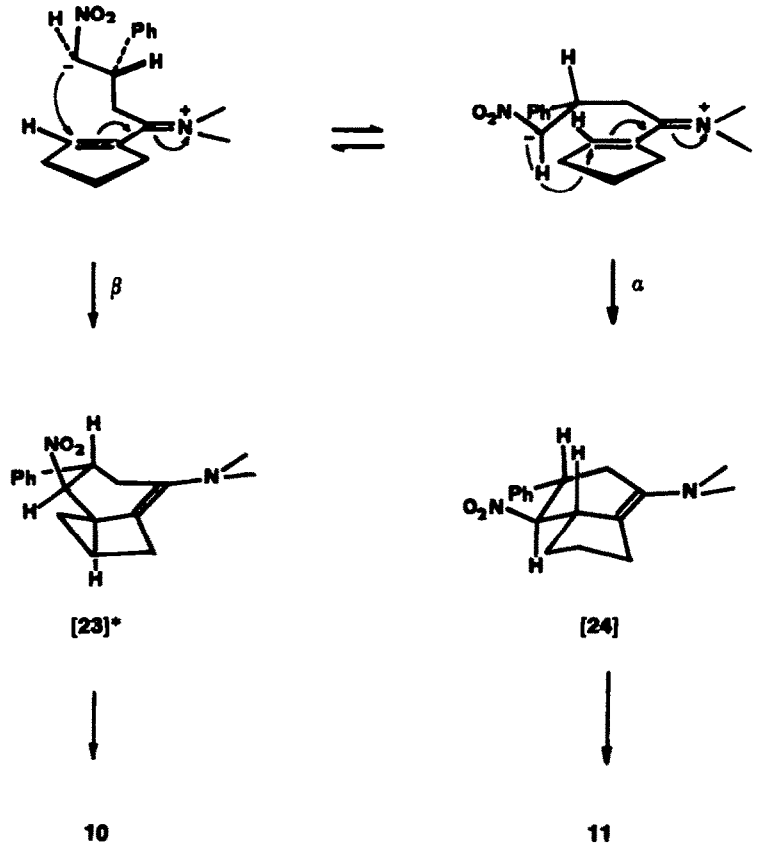
Fig. 1. MX part of the ABMX spin-system of compounds 15, 16 and 17 respectively.

Enamine **26** was assigned the structure of 4 - morpholino - 1,3a,5,6,7,7a - hexahydrocyclopenta[c]thiopyrane 2,2-dioxide, on the basis of IR and NMR data. The IR spectrum in fact showed the enamine double bond absorption at 1560 cm^{-1} and the NMR spectrum showed the vinylic proton singlet at 5.1 δ. No other vinylic proton signal appeared in the spectrum. Hydrolysis of **26** yielded the corresponding ketone **29**, which did not undergo equilibration in either acidic or basic medium. Also **26** was a product of thermodynamic control, as the compound of kinetic control would have been the more substituted isomer, which was not isolated.

In fact, also in this case the mechanism would involve a non-concerted attack of sulphene on the β-carbon of **2** to give a zwitterionic intermediate.[1] Nucleophilic attack of the carbon anion onto the electrophilic centre of the cyclopentene ring would lead to the tetrasubstituted compound which rapidly isomerized, owing to the above mentioned $A^{(1,3)}$ strain.

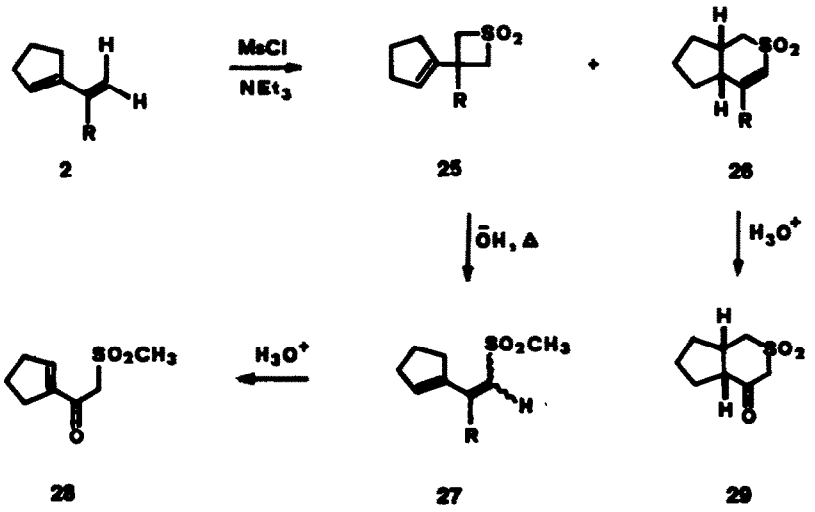
The *cis* fusion was attributed to the compound **26**, in accordance with other authors[13] who attributed the same geometry to an analogous compound. The same conclusion is arrived at from the fact that the corresponding ketone **29** did not equilibrate. In comparison with the hexahydro-hydrindan-4-one system,[4] insertion of an SO_2 group with consequent enlargement of the 6-membered ring would further favour the *cis* fusion, as clearly indicated by inspection of the Dreiding models.

Finally a question arises as to the reason why in the analogous reaction of 1-(cyclohexen-1-yl)-morpholino ethene the [4+2]cycloaddition did not take place.[1] We think this could be due to the differing contributions to the stability of the intermediates from the respective alicyclic rings. It is known that both cyclopentyl[14] and cyclopnetenyl[15] cations are more stable than the cyclohexyl and cyclohexenyl cations respectively. Since in the intermediates the alicyclic part has a certain carbonium ion character, this would result in a lesser stability of the 6-membered ring intermediate, with consequent immediate neutralization of the negative charge onto the closest electrophilic centre. However, in the more stable



*Compounds in brackets were not isolated

Scheme 3.



R = morpholino–

Scheme 4.

5-membered ring intermediate a conformational change would be possible so as to allow the carbonium anion to orientate towards the electrophilic ring centre.

EXPERIMENTAL

M.ps were determined on a Gallenkamp apparatus and are uncorrected. IR spectra were recorded as mulls (Nujol) on a Perkin–Elmer 257 spectrometer. UV spectra were recorded on a Perkin–Elmer 124 spectrophotometer. NMR spectra were recorded on a JNM-60-HL Jeol spectrometer in $CDCl_3$ solns, unless otherwise stated, using TMS as internal standard. The nomenclature followed the rules indicated by Chemical Abstracts. Columns were prepared using extra pure SiO_2 Merck (70–325 mesh ATMS).

Synthesis of the parent enamines. Enamine **1** was prepared from cyclopentyl-methyl-ketone and morpholine by the White and Weingarten method, [16] b.p.$_{.18\ mmHg}$ 115–20°. ν_{max} cm^{-1} 1680 (C=C), 1645 (C=C–N), 1110 (CH_2OCH_2). NMR, δ 2.65 (CH_2NCH_2, 4H, m); 3.68 (CH_2OCH_2, 4H, m); 3.85, 4.02 (C=CH_2, 2H, 2s). Enamine **2** was prepared from (cyclopenten-1-yl)-methyl-ketone[17]† and morpholine, b.p.$_{3\ mmHg}$ 90–2°. ν_{max}(cm^{-1}) 1660, 1610 (C=C–C=C), 1112 (CH_2OCH_2). NMR, δ 2.85 (CH_2NCH_2, 4H, m); 3.75 (CH_2OCH_2, 4H, m); 4.18, 4.35 (C=CH_2, 2H, 2s); 5.90 (C=CH, 1H, m).

Reaction of **1** *with β-nitrostyrene.* β-Nitrostyrene (1.8 g, 10 mmol) in dry ether was added to **1** (1.8 g, 10 mmol) in ether, at 5°. After 72 h, removal of the solvent left an orange oily residue, **3**, which showed δ 2.4 (CH_2CHPh, 2H, m); 2.8 (CH_2NCH_2, 4H, m); 3.8 (CH_2OCH_2, CHPh, 5H); 4.6 (CH_2NO_2, 2H, m); 7.3 (Ph, 5H, m). ν_{max} (cm^{-1}) 1650 (C=C–N); 1600, 1575, 755, 690 (Ph), 1545, 1340 (NO_2), 1110 (CH_2OCH_2).

Hydrolysis of **3**. Dil. HCl and enamine **3** in equal amounts were mixed up in methanol at r.t. After a few hours the solvent was removed and the residue extracted with ether. The oil was crystallized with light petroleum, m.p. 40–1° (Found for its 2,4-dinitrophenylhydrazone derivative, m.p. 143–4°, from ethanol: C, 57.4; H, 5.25; N, 15.60. $C_{21}H_{23}N_5O_6$ requires: C, 57.1; H, 5.25; N, 15.86%). NMR, δ 1.60 (CH_2, 8H); 2.90 (CH_2CO, 2H, d); 4.00 (CHPh, 1H, m); 4.65 (CH_2NO_2, dd, 2H); 7.30 (Ph, 5H, m). ν_{max} (cm^{-1}) 1705 (CO), 1600, 1580, 760, 690 (Ph), 1545 (NO_2).

Reaction of **1** *with mesyl chloride.* A soln of mesyl chloride (3.7 g, 32 mmol) in dry ether was added dropwise, under stirring to a mixture of **1** (5.8 g, 32 mmol) and triethylamine (3.2 g, 32 mmol) in the same solvent, at 5°. The triethylamine hydrochloride salt was filtered off and the ethereal soln was allowed to stand at 5° for 48 h. A white crystalline ppt separated, **5** (3.0 g, 37%), m.p. 123°, from benzene–*n*–hexane (Found: C, 55.9; H, 8.01; N, 5.51. $C_{12}H_{21}NO_3S$ requires: C, 55.6; H, 8.16; N, 5.40%). ν_{max} (cm^{-1}) 1285, 1260, 1100 (SO_2), 1115 (CH_2OCH_2). NMR, δ 1.45 (CH_3, 3H, s); 2.4 (CH_2NCH_2, 4H, m); 3.6 (CH_2SO_2, 2H, s); 3.7 (CH_2OCH_2, 4H, m). 3.6 (CH_2SO_2, 2H, s); 3.7 (CH_2OCH_2, 4H, m). The mother liquors were extracted and chromatographed on SiO_2. A further 2.2 g (27%) of **5** were obtained together with a small amount (about 5% each) of **6** and **7**. Compound **6** could not be completely purified, ν_{max}(cm^{-1}) 1310, 1180 (SO_2); 1135 (CH_2OCH_2). NMR, δ 2.65 (CH_2NCH_2, 4H, m);3.7 (CH_2OCH_2, 4H, m); 4.0 ($CH_2SO_2CH_2$, 4H, m). The remaining 30% was mesylmorpholide **8**.

Hydrolysis of **6**. Dil.HCl and **5** were mixed up in acetone and refluxed for 48 h. A semisolid material, **9**, was recovered and purified on a column, ν_{max}(cm^{-1}) 1710 (CO); 1317, 1145 (SO_2). NMR, δ 2.55 (CHCO, 1H, bm); 3.0 (SO_2CH_3, 3H, s); 4.0 (CH_2SO_2, 2H, s).

Reversibility of **6**. A quantity of **6** was refluxed in morpholine for 15 h. It was completely converted into mesylmorpholide **8**.

Reaction of **2** *with β-nitrostyrene.* β-Nitrostyrene (1.7 g, 12.2 mmol) in dry ether was added to a soln of **2** (2.0 g, 12.2 mmol) in the same solvent. After 72 h of standing at 5°, large colourless crystals separated (1.5 g, 4.6 mmol), **10**, m.p. 105–6°, from benzene–*n*–hexane (Found: C, 69.2, H, 7.18, N, 8.56. $C_{19}H_{24}N_2O_3$ requires: C, 69.5; H, 7.37; N, 8.53%). NMR, δ 2.85 (CH_2NCH_2, H-3a, H-7a, 6H, m); 3.75 (CH_2OCH_2, 4H, m); 4.2 (CHPh, 1H, m); 4.4 (C=CH, 1H, d, J = 2.0 Hz); 4.8 ($CHNO_2$, 1H, dd, J_{67} = 10.5 Hz; J_{77a} = 3.75 Hz); 7.35 (Ph, 5H, m). ν_{max}(cm^{-1}) 1620 (C=C–N), 1540, 1365, (NO_2), 1115 (CH_2OCH_2), 1600, 760, 698 (Ph). The mother liquors were hydrolysed and extracted. Evaporation of the solvent gave an orange oily residue which was chromatographed on SiO_2. Elution with benzene gave ketones **15** (0.65 g, 2.5 mmol), **16** (0.3 g, 1.2 mmol), **18** (0.3 g, 1.2 mmol) and **19** (0.35 g, 0.9 mmol). Ketone **15** was also obtained from the hydrolysis of **10** carried out in a mixture acetone: water: dil. HCl, for 2 h. Ketone **15** was crystallized from benzene–*n*–hexane, m.p. 130–1° (Found: C, 69.1; H, 6.59; N, 5.32. $C_{15}H_{17}NO_3$ requires: C, 69.5; H, 6.61; N 5.40%). NMR ($CDCl_3$), δ 2.5 (H–3, 1H, m); 2.6 (CH_2CO, 2H, dd); 2.95 (H–3a, H–7a, 2H, m); 3.8 (CHPh, 1H, m); 5.5 ($CHNO_2$, 1H, dd); 7.2 (Ph, 5H, m). NMR (C_6D_6), δ 2.25 (CH_2CO, two pseudo-AB quartets, J_{AB} = −14.2 Hz, J_{AM} = 12.7 Hz, J_{BM} = 5.2 Hz); 3.5 (CHPh, 1H, J_{AM} = 12.7 Hz, J_{BM} = 5.2 Hz, J_{MX} = 11.6 Hz); 5.0 ($CHNO_2$, 1H, dd, J_{MX} = 11.6 Hz, J_{XH-7a} = 5.0 Hz); 7.0 (Ph, 5H, m). ν_{max}(cm^{-1}) 1720 (CO), 1545, 1365 (NO_2), 1600, 1580, 760, 695 (Ph). Ketone **16** had m.p. 143–5°, from benzene-*n*-hexane (Found: C, 69.6; H, 6.85; N, 5.12. $C_{15}H_{17}NO_3$ requires: C, 69.5; H, 6.61; N, 5.40%). NMR ($CDCl_3$), δ 2.7 (CH_2CO, 2H, m); 3.0 (H–3a, H–7a, 2H, m); 3.7 (CHPh, 1H, m); 4.7 ($CHNO_2$, 1H, dd); 7.3 (Ph, 5H, m). NMR (C_6D_6), δ2.25 (CH_2CO, 2H, m); 2.5 (H–3a, H–7a, 2H, m); 3.25 (CHPh, 1H, m, J_{MX} = 11.2 Hz, $J_{AM}+J_{BM}$ = 18.7 Hz); 4.4 ($CHNO_2$, 1H, dd, J_{MX} = 11.2 Hz, J_{XH-7a} = 10.3 Hz); 7.1 (Ph, 5H, m). ν_{max}(cm^{-1}) 1700 (CO), 1550, 1352 (NO_2), 1600, 1585, 755, 695 (Ph). The open chain ketone **18** was crystallized from benzene–*n*–hexane, m.p. 85–9° (Found: C, 69.7; H, 6.37; N, 5.64. $C_{15}H_{17}NO_3$ requires: C, 69.5; H, 6.61; N 5.40%). NMR, δ 2.9 (CH_2CO, 2H, m); 4.1 (CHPh, 1H, m); 4.7 (CH_2NO_2, 2H, dd); 7.3 (Ph, C=CH, 6H, m). $\nu_{max}^{CHCl_3}$(cm^{-1}) 1710 (CO), 1548 1370 (NO_2), 1600, 690 (Ph). The ketone **19**, identified as 6,8 - diphenyl - 7,9 - dinitro - [6.3.0]bicycloundecan - 4 - one, had m.p. 180–2°, from benzene-*n*-hexane (Found: C, 67.9; H, 5.70; N, 6.41. $C_{23}H_{24}N_2O_5$ requires: C, 67.6; H, 5.92; N, 6.86%). NMR, δ 2.1 (CH_2, 6H); 2.6 (H–3a, H–9a, 2H); 3.0 (CHPh, 1H, m); 3.6 (CH_2CO, 2H, m); 4.6 ($CHNO_2$, 2H, m); 6.9 (aromatic protons, 4H, m); 7.3 (aromatic protons, 6H, m). ν_{max}(cm^{-1}) 1695 (CO), 1550, 1535 (NO_2), 1600, 1580, 745, 715, 688 (Ph). The total yield was 85%.

Reaction of **2** *with β-nitrostyrene in absolute ethanol.* The above reaction was repeated in absolute ethanol. After 24 h at 5°, enamine **14** was separated (0.15 g, 0.3 mmol), m.p. 208–10°. NMR, δ 2.8 (CH_2NCH_2, 4H, m); 3.7 (CH_2OCH_2, 4H, m); 4.4 ($CHNO_2$, C=CH, 3H, m); 7.2 (Ph, 10H, m). ν_{max}(cm^{-1}) 1615 (C=C–N), 1540 (NO_2), 1600, 762, 710, 690 (Ph), 1110 (CH_2OCH_2). Acidic hydrolysis of **14**, carried out in acetone: water: dil. HCl led to the corresponding ketone **20**, 6,8 - diphenyl - 7,9 - dinitro - [6.3.0]bicycloundecan - 4 - one, m.p. 164–5°, from benzene-*n*-hexane (Found: C, 67.3; H, 5.72; N, 6.84. $C_{23}H_{24}N_2O_5$ requires: C, 67.6; H, 5.92; N, 6.86%). NMR, δ 2.2 (CH_2, 10H, m); 3.3 (CHPh, 2H, m); 4.6 ($CHNO_2$, 2H, m); 7.25 (Ph, 10H, m). ν_{max}(cm^{-1}) 1695 (CO), 1542 (NO_2), 1598, 760, 715, 700, 690 (Ph). The mother liquors were concentrated and by scratching enamine **11** was isolated, (0.95 g, 2.9 mmol) m.p. 149–52°, from benzene-*n*-hexane (Found: C, 69.3; H, 7.51; N, 8.30. $C_{19}H_{24}N_2O_3$ requires: C, 69.5; H, 7.37; N, 8.53%). NMR, δ 1.8 (CH_2, 6H, m); 2.8 (CH_2NCH_2, H–3a, H–7a, 6H, m); 3.7 (CH_2OCH_2, 4H, m); 4.3 (CH_2NO_2, C=CH, CHPh, 3H, m); 7.3 (Ph, 5H, m). ν_{max}(cm^{-1}) 1622 (C=C–N), 1600, 1580, 760, 692 (Ph), 1536, 1345 (NO_2), 1115 (CH_2OCH_2). The mother liquors were hydrolysed, extracted and chromatographed on SiO_2. Elution with benzene yielded **15** (0.95 g, 3.8 mmol), **16** (0.75 g, 3.0 mmol), **20** (0.2 g, 0.5 mmol), and **19** (0.1 g, 0.25 mmol). The total yield was about 85%. Enamine **11** underwent rapid hydrolysis to the corresponding ketone **16**.

Equilibration of **16**. Ketone **16** was refluxed with TsOH in benzene for 3 h. A 8:2 mixture of **17** and **16** was obtained. The two stereoisomers were separated chromatographically, **17**, m.p. 148–50°, from benzene-*n*-hexane (Found: C, 69.3; H, 6.48; N, 5.31. $C_{15}H_{17}NO_3$ requires: C, 69.5; H, 6.61; N, 5.40%). NMR, δ 2.6 (CH_2CO, 2H, m); 3.65 (CHPh, 1H, m, $J_{AM}+J_{BM}$ = 18.7 Hz,

†(Cyclopenten-1-yl)-methyl-ketone was separated from 1-acetyl-2-chloro-cyclopentane by means of the Perkin-Elmer 251 spinning band apparatus.

J_{MX} = 10.5 Hz); 4.9 ($CH\underline{H}NO_2$, 1H, dd, J_{MX} = 10.5 Hz, J_{XH-7a} = 9.7 Hz); 7.2 (Ph, 5H, m). ν_{max}(cm^{-1}) 1710 (CO), 1545 (NO_2), 1600, 1580, 760, 715, 690 (Ph).

Basic treatment of **15**. Ketone **15** in absolute EtOH was added to NaOH in EtOH, in ratio 1:1. After 30 min CH_3COOH was added to pH = 6. Ketone **21** separated as white needles, m.p. 134°, from benzene-*n*-hexane (Found: C, 69.8; H, 6.50; N, 5.15. $C_{15}H_{17}NO_3$ requires: C, 69.5; H, 6.61; N, 5.40%). NMR (C_6D_6), δ 1.25 (CH_2, 4H, m); 2.3 (H–3, H–3a, H–7a, 3H, m); 2.85 ($CH\underline{H}Ph$, 1H, m, W_H = 13.5 Hz); 3.15 ($CH\underline{H}CO$, 2H, m); 4.5 ($CH\underline{H}NO_2$, 1H, dd, J_1 = 3.0 Hz, J_2 = 3.4 Hz); 7.1 (Ph, 5H, m). ν_{max}(cm^{-1}) 1700 (CO), 1550 (NO_2), 1600, 1585, 792, 745, 695 (Ph).

Basic treatment of **16**. Ketone **16** was added to an equimolar amount of NaOH in abs. EtOH. After complete dissolution, acetic acid was added to pH = 6. A ppt. formed, **22**, m.p. 120°, from benzene-*n*-hexane. NMR, δ 1.8(CH_2, 6H); 2.75 ($CH\underline{H}CO_2$, 2H, aq); 3.6 ($CH\underline{H}Ph$, 1H, m, W_H = 13.5 Hz); 5.0 ($CH\underline{H}NO_2$, 1H, dd, J_1 = 3.0 Hz, J_2 = 5.5 Hz); 7.2 (Ph, 5H, m). ν_{max}(cm^{-1})1695 (CO), 1540 (NO_2), 1600, 750, 715, 690 (Ph).

Reaction of **2** *with mesyl chloride*. The reaction was performed as indicated above for enamine **1**. After removal of the solvent, the oily residue was treated with *n*-hexane on heating, in orde to eliminate the morpholide **8** which is insoluble in *n*-hexane. From the resulting soln. a mixture of **25** and **26** precipitated. The two products were separated by fractional crystallization, **25**, m.p. 156–7°, from benzene-*n*-hexane (Found: C, 56.3; H, 7.75; N, 5.54. $C_{12}H_{19}NO_3S$ requires: C, 56.0, H, 7.44; N, 5.44%). ν_{max}(cm^{-1}) 1310, 1100 (SO_2), 1120 (CH_2OCH_2). NMR, δ 2.5 ($CH\underline{H}NCH_2$, $CH\underline{H}$ 10H, m); 3.75 ($CH\underline{H}OCH_2$, 4H, m); 4.25 ($CH\underline{H}SO_2$, 4H, m); 5.80 (C=C$\underline{H}$, 1H, m). Compound **26**, m.p. 155–8°, from benzene-*n*-hexane (C, 56.4; H, 7.14, N, 5.44. $C_{12}H_{19}NO_3S$ requires: C, 56.0; 7.44; N, 5.44%). ν_{max}(cm^{-1}) 1560 (C=C–N); 1260, 1100 (SO_2), 1090 (CH_2OCH_2). NMR, δ 1.8 ($CH\underline{H}$, 6H, sharp m); 2.9 ($CH\underline{H}SO_2$, 2H, m); 3.0 ($CH\underline{H}NCH_2$, H–4a, H–7a, 6H, m); 3.70 ($CH\underline{H}OCH\underline{H}$, 4H, m); 5.1 (C=C$\underline{H}$, 1H, s). The mother liquors were hydrolysed, extracted and the components separated on SiO_2, in order to determine the total yield. Further amount of **25** was obtained together with **29**, m.p. 131–3°, from benzene-*n*-hexane (Found: C, 51.3; H, 6.26. $C_8H_{12}O_3S$ requires: C, 51.0; H, 6.43%). ν_{max}(cm^{-1}) 1715 (CO), 1315, 1295, 1115, 1105 (SO_2). NMR, δ 1.9 ($CH\underline{H}$, 7H, m); 3.3 ($CH\underline{H}SO_2$, H–3a, H–7a, 4H, bm); 4.0 ($SO_2CH\underline{H}CO$, 2H, m). The total yield was 83% and the ratio **25**:**26** was 4:3.

Hydrolysis of **26**. Acidic hydrolysis of **26** was performed in a mixture acetone: water: acetic acid at pH 6. After 2 h the reaction was complete and **29** was separated.

Basic treatment of **25**. A small amount of **25** was added to a soln of KOH in abs. EtOH and refluxed for 4 days. The mixture was extrated repeatedly with ether and benzene. The ethereal extracts contained **27** exclusively, whereas the benzenic extracts contained a mixture of **27** and **28**. Enamine **27** was thus isolated, m.p. 100–2°, but could not be purified. ν_{max}(cm^{-1}) 1630 (C=C), 1560 (C=C–N), 1370, 1130, 1120, (SO_2), 1110 (CH_2OCH_2). NMR, δ 2.9 (SO_2CH_3, 3H, s); ($CH_2NCH\underline{H}$, 4H, m); 3.7 ($CH\underline{H}OCH\underline{H}$, 4H, m); 5.1 (N–C=C$\underline{H}$, 1H, s); 5.9 (C=C$\underline{H}$, 1H, m).

Hydrolysis of **27**. A small amount of **27** was hydrolysed in acetone: water, at r.t. for 2 h. A white semisolid material precipitated, **28**, ν_{max}(cm^{-1}) 1660 (C=O), 1535 (C=C), 1320, 1300, 1110 (SO_2). NMR, δ 3.0 (CH_3SO_2, 3H, s) 4.3 ($CH\underline{H}SO_2$, 2H, s); 6.9 (C=C$\underline{H}$, 1H, m).

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