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ENAMINE CHEMISTRY—XXIV.[a]

SYNTHESIS, THIATION, AND REDUCTION OF LACTAMS

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Abstract—Enamines, **1**, prepared from cyclohexanones or cyclopentanones are reacted with acrylamide to give lactams, the condensed 2-piperidones, **2**. Ethyl 2-(1-pyrrolidinyl)-2-cyclohexene-1-propanoate, **3**, when treated with primary amines, produces the corresponding N-substituted 2-piperidones, **4**. Ethyl 2-(1-pyrrolidinyl)-2-cyclohexene-1-ethanoates and ethyl 2-(1-pyrrolidinyl)-2-cyclopentene-1-ethanoate, **5**, react with primary amines to give condensed N-substituted 2-pyrrolidones, **6**, and non-cyclic imines, **7**. The starting enamines, **1**, treated with 2-bromo acetamides only afford the N-alkylated compounds, **8** (2-pyrrolidino acetamides), and the regioselectivity of this reaction is rationalized in terms of the HSAB-principle. Compound **1** undergoes an exchange reaction (aminolysis) when reacted with primary amines to give the imines **9**. Thiation of the lactams **2** and **6** with the Lawesson reagent (LR), affords the corresponding thiolactams, **10**. Reduction of the lactams and thiolactams, **2**, **6**, and **10** by LAH gives the imines, **11**, and the enamines, **16**. Further reduction of **11** (LAH) affords the saturated amines, **15**. The stereochemistry for the formation of **15** is discussed using the torsion angle notation and the principal of least torsional distortion. In a one-pot reaction using LAH-acetic anhydride the lactams, **2**, and the thiolactams, **10**, are transformed into the enamides, **14**. Compound **14** was also obtained from **11** by direct acetylation with acetic anhydride in the presence of triethylamine.

Enamines are of great importance in synthesis and undergo a variety of reactions.[1-3] We have been interested in alkylation and Michael addition reactions of enamines and in the subsequent Stevens, Hoffmann and reductive cyclisation reactions.[4-8] (Scheme 1). As a continuation, attempts have been made to find new routes to condensed N-heterocycles by reaction of enamines with electrophiles containing an amide functional group, followed by reduction. This publication reports on syntheses of lactams and thiolactams and on reduction and reductive acylation of these substrates.

The starting enamines, **1** were prepared according to known methods.[2,7,8] By refluxing **1** with acrylamide,[9,10] **2**, were smoothly formed in high yields. The enamines, **1**, were expected to undergo a Michael addition giving the normal alkylation products [2]. However, subsequent ring closure under elimination of pyrrolidine to give **2** was observed. The lactams, **2**, were characterised by IR, MS, ^{1}H and ^{13}C NMR spectroscopy, microanalyses, and were also in some cases identified with authentic material.[11] Compounds **2a** and **2b** were mixtures of isomers, 3,4,4a,5,6,7 - hexahydro - 2(1 H) - quinolone and 3,4,5,6,7,8 - hexahydro - 2(1 H) - quinolone, in contrast to compound **2d**, in which case only $\Delta^{4a(7a)}$ - hexahydro - 2(1 H) - pyrindone, was isolated (Table 1). The enamines, **1**, were also treated with crotylanilide but no reaction took place.†

Attempts to prepare amides with an enamine function, **8'** by reacting **1** with 2 - bromocarboxamides (2 -

[a]Part XXIII, J. B. Rasmussen, R. Shabana, and S.-O. Lawesson, *Tetrahedron* **37**, 3693 (1981).

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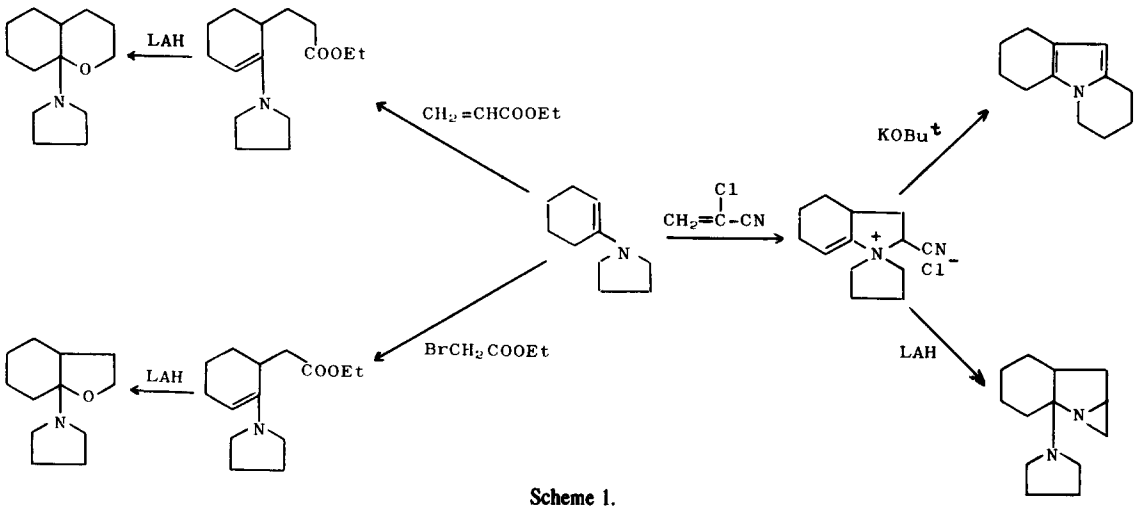
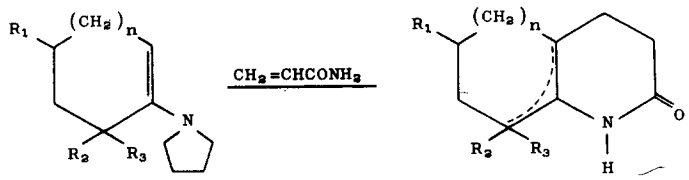
†For a few earlier reports on Michael additions to α,β-unsaturated amides see Ref. 12.



Scheme 1.

Table 1. Physical and spectroscopic data of 2. 1 → 2



1 2

2	Yield (%)	B.p.(°C/torr) M.p.(°C)	^{1}H NMR (δ) H-C=C	NH	^{13}C NMR (δ) C=O	C=C-N	C=C-N
a*	100	110/0.2 142	5.1(s, 0.5 H)	8.2(s, 0.5H) 8.9(s, 0.5H)	175.0 169.8	135.6 127.8	108.2 102.7
b*	90	130	4.95(s, 0.4H)	8.4(s, 0.6H) 9.2(s, 0.4H)	174.5 170.1	134.7 127.6	107.5 101.3
c**	73	-	-	8.2(s, 1H)	170.1	131.8	107.8
d**	85	120/0.4 102	-	8.65(s, 1H)	172.3	137.8	116.2
e**	72	192	-	8.9(s, 1H)	171.5	141.6	113.2

Solvent: Dioxane*, benzene**. 2e: ^{1}H NMR (δ): 1.22 (s, 3H), 1.18(s, 3H), 1.07(s, 3H). Analyses (C, H, N).

bromoacetanilide and 2-bromo-N-cyclohexyl-acetamide), similar to the C-alkylation of **1** by 2-bromocarboxylic esters,[8,13] resulted unexpectedly in the formation of 2-pyrrolidino-acetamides, **8**. This reaction performed at room temperature or at reflux in anhydrous benzene or toluene for several hr yielded only the compounds **8** in high yields. In order to elucidate the mechanism for the formation of **8**, the reaction was followed by glc, which showed that cyclohexanone was produced and no traces of cyclohexane, cyclohexene, cyclohexadiene or benzene were detected. The first step must be substitution on nitrogen to give the enammonium salt[8], which subsequently by some humidity was transformed into 2-pyrrolidino-acetamides, **8**, and cyclohexanone (0.18 g H_2O is sufficient for a complete hydrolysis). An authentic sample of N-cyclohexyl-2-(1-pyrrolidinyl)-acetamide was prepared from excess (2 moles) of pyrrolidine with 2 - bromo - N - cyclohexyl-acetamide. Finally, the substitution with the ambident enamine, **1**, can be rationalized in terms of hard and soft acid-base theory.[34] The N atom of **1** is classified as a "hard base" while the β-C in the same molecule is a "soft base". The α-C atom in ethyl bromoacetate must be regarded as soft (less hard) as it substitutes the enamines on the C-atom (Scheme 1). In α-bromocarboxamides the α-C atom must be quite as hard as it only produces the N-substitution product. Thus the regioselective reactions (also ethyl bromoacetate[8]) can be rationalised by the preferential reaction of hard acids with hard bases and soft acids with soft bases.

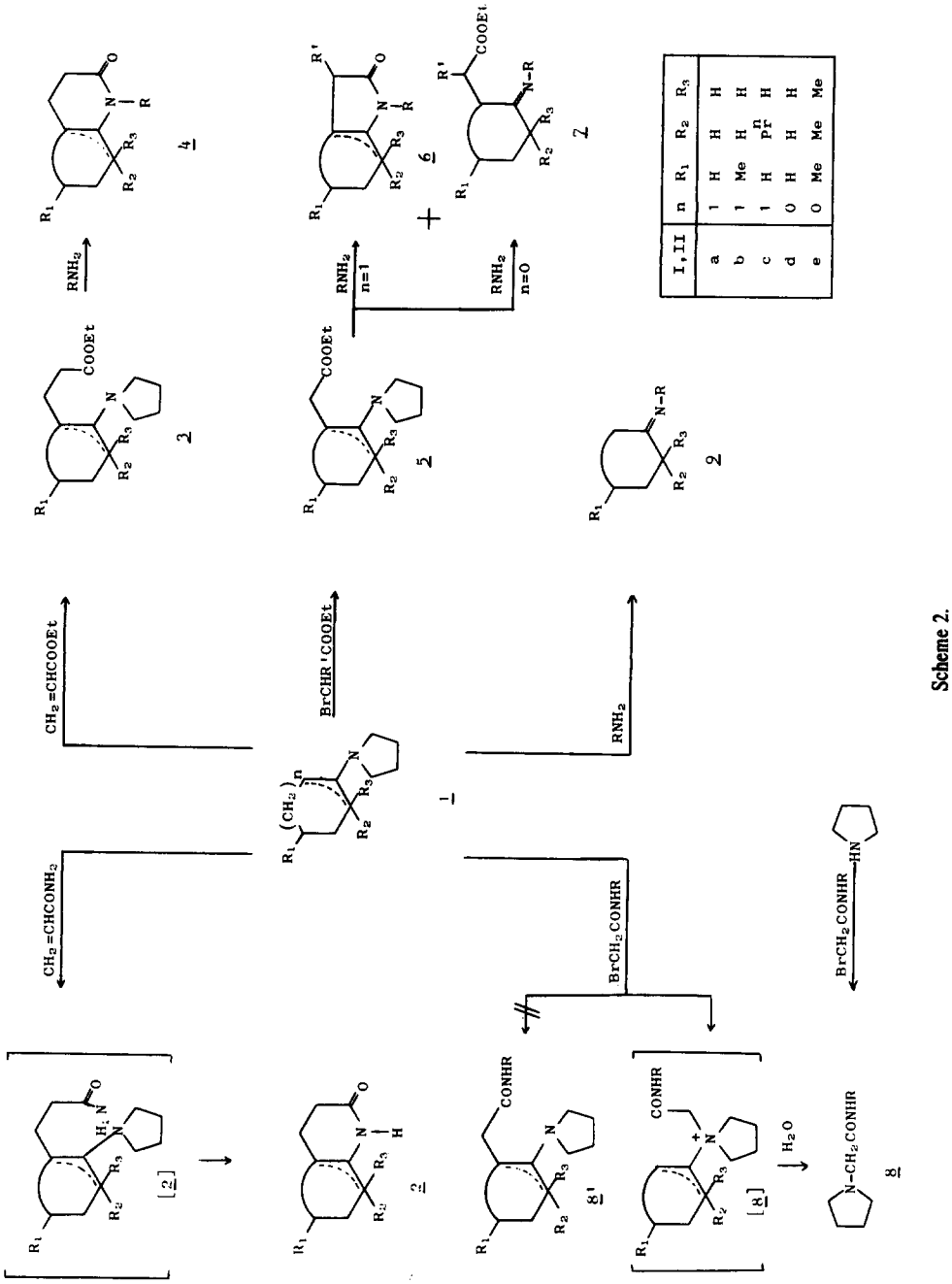
As an alternative route to 5- and 6-membered lactams, the enamines **3** and **5** were reacted with primary amines (n - propylamine, cyclohexlamine and benzylamine) yielding N - substituted piperidones, **4**, and pyrrolidones, **6**. It is suggested that the reaction proceeds through transamination (aminolysis) of **3** and **5** followed by a ring closure giving the lactams **4** and **6**. This mechanism is supported by the formation of the benzylimines **9**, from the reaction of benzylamine with the starting enamines, **1**. Reaction of ethyl 2-(1-pyrrolidinyl-2-cyclopentene-1-acetate with benzylamine afforded the non-cyclic iminoester, **7** (ethyl 2 - benzylimino - cyclopentane - 1 - acetate). The tetrahydroindolones, **6**, are mixtures of the isomers $\Delta^{7(7a)}$-tetrahydro-2-indolone, **6a**, and $\Delta^{3a(7a)}$-tetrahydro-2-indolone, **6b**. In two cases, **6.1** and **6.3**, both isomers were separated by column chromatography. The two isomers were easily differentiated by ^{1}H and ^{13}C NMR spectroscopy. The $\Delta^{7(7a)}$-isomer exhibits carbon resonances at 176.7 (C=O), 140.5 (C=C-N) and 96-7 (C=C-N). The corresponding shifts for the $\Delta^{3(7a)}$-isomers are found at 171.9 (C=O), 151-2 (C=C-N) and 124 (C=C-N). All the lactams **4** and **6** were characterised by IR, MS, ^{1}H and ^{13}C NMR spectroscopy (Table 2).

Thiation of lactams. 2,4 - Bis(4 - methoxyphenyl) - 1,3,2,4 - dithiaphosphetane - 2,4 - disulfide (LR), is a most effective thiation reagent for a variety of functions.[15-26] It (LR) is easily available, and has been found to react with the lactams **2** and **6** giving in most cases quite good yields of the thiolactams, **10** (Scheme 3, Table 3).

The starting lactams, **2a** and **2b**, both of which are mixtures of isomers yield only the $\Delta^{4a(8a)}$-isomer **10'**, after thiation (no vinylic hydrogens observed in ^{1}H NMR). Thiation of the lactams **2c-2e** and **6.1a** gave the expected thiolactams (no isomerisation of the C=C double bond was observed). The structure of the thiolactams **10** was proved by IR, MS, ^{1}H and ^{13}C NMR and microanalyses.†

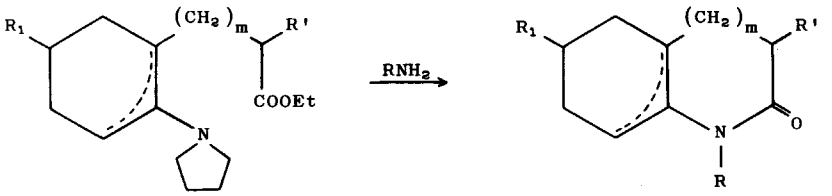
Reduction of lactams and thiolactams. LAH reduces carboxamides and lactams to amines[28,29] (although C-N cleavage of teriary amides are frequently observed at

†^{13}C NMR, see Ref. 27. Related compounds have been prepared earlier.[25]


CH2=CHCOOEt
BrCHR'COOEt
RNH2
CH2=CHCONH2
BrCH2CONHR
Br-CH2CONHR
RNH2 n=1
RNH2 n=0
H2O
I, II
a
b
c
d
e
n
R1
R2
R3
1 H H H
1 Me H H
1 H Pr n H
0 H H H
0 Me Me Me

Scheme 2.

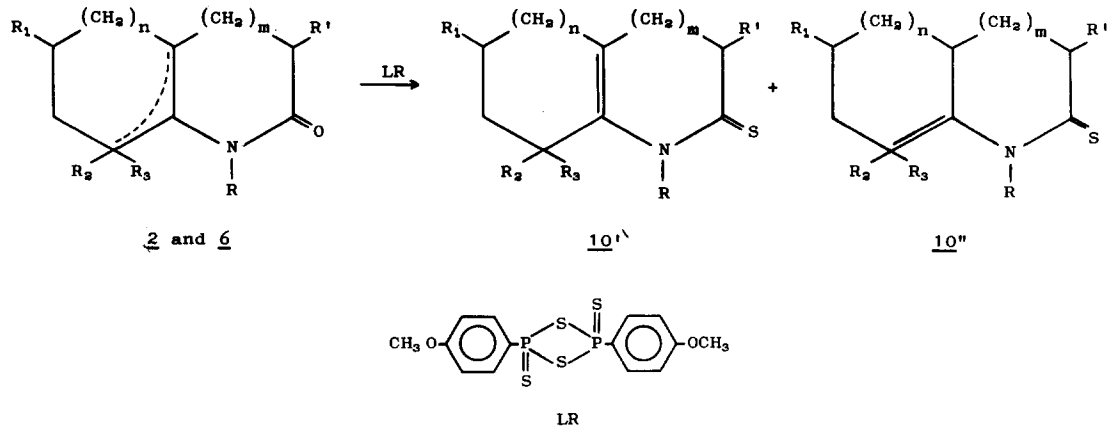
Table 2. Spectroscopic data of the lactams 4 and 6. 3 and 5→4 and 6



3 and 5 — 4 and 6

	m	R_1	R'	R	Solvent	React. temp. (°C)	React. time (hr)	Yield (%)	^{1}H NMR (δ) H-C=C	^{1}H NMR (δ) CH_2-N	^{13}C NMR (δ) C=O	^{13}C NMR (δ) C=C-N	^{13}C NMR (δ) C=C-N
4	1	H	H	$PhCH_2$	DMF	150	15	16	5.2(s, 1H)	4.8(s, 2H)	170.2	138.5	115.0
6.1a	0	H	Me	Pr^n	benzene	80	10	52	4.9(s, 1H)	3.5(m, 2H)	176.7	140.7	96.1
6.1b*	0	H	Me	Pr^n	benzene	80	10	42	-	3.6(m, 2H)	171.8	151.9	124.2
6.2	0	H	Me	C_6H_{11}	dioxane	100	10	52	4.95(s, 1H)	4.1(m, 1H)	176.5	146.5	97.1
6.3a	0	H	Me	$PhCH_2$	benzene	80	20	34	4.8(s, 1H)	4.6(s, 2H)	176.9	140.2	97.3
6.3b	0	H	Me	$PhCH_2$	benzene	80	20	50	-	4.7(s, 2H)	172.0	152.8	124.1
6.4	0	Me	Me	$PhCH_2$	DMF	150	10	32	4.8(s, 0.1H)	4.6(s, 2H)	171.9	151.7	123.9

* Precise measurement on $M^{\oplus}$ (calc. for $C_{12}H_{19}NO$: 193,1465, found: 193,1448).

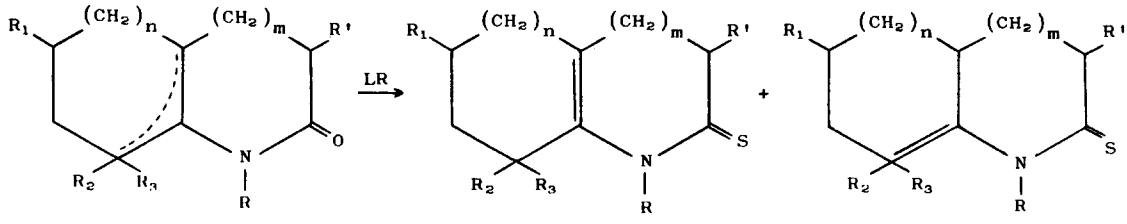


2 and 6 10' 10"

LR

Scheme 3.

Table 3. Thiation conditions and spectroscopic data of 10' and 10". 2,6→10'+10"



2 and 6 10' 10"

Start.	Product	React. temp. (°C)	Yield (%)	M.p. (°C)	^{1}H NMR (δ) NH	^{1}H NMR (δ) CHR'-CS	^{13}C NMR (δ) C=S	^{13}C NMR (δ) C=C-N	^{13}C NMR (δ) C=C-N
2a	10'a	25	65	140	10.2	2.9(t, J = 6Hz, 2H)	197.3	128.7	115.7
2b	10'b	80	50	112	10.1	2.9(t, J = 7Hz, 2H)	197.7	128.5	115.4
2c	10'c	25	82	-	9.9	2.85(m, 2H)	197.4	129.9	117.1
2d	10'd	25	60	140	10.0	3.1(t, J = 7Hz, 2H)	198.2	133.3	119.8
2e	10'e	25	69	135	9.9	2.85(m, 2H)	199.1	139.8	121.4
6.1a	10"f	25	20	-					

10"f. ^{1}H NMR: 6.25(s, 1H, H-C=C), 3.6(t, J = 7Hz, 2H, CH_2N). MS (rel.int.%): 209 (M^+, 21), 177(75), 162(23), 149(100), 134(32), 120(23), 107(38), 91(8), 43(8). 10'd: Analyses (C, H, N, S).

low temperature[30-32]). The 2-piperidones, **2**, when treated with excess of LAH for 3 hr were reduced to the imines, **11**. The compounds **11**, are sensitive to oxygen and humidity and transformed into the hydroperoxide,[33] **12**, and the semiaminal, **13**, respectively. Reductive acetylation of the lactams, **2**, afforded the stable enamides, **14**. The acetylation was performed by excess acetic anhydride before decomposition at low temperature (−15°) and the reduction by LAH may proceed via the intermediate enamine salt[11], which subsequently was acetylated on N in agreement with the HSAB principle.[34] The enamides **14** were also obtained from **11** by acetylation. This one-pot conversion of lactams to acetamides, see Ref. 35, appears to be of wide scope for the protection of sensitive nitrogen compounds.

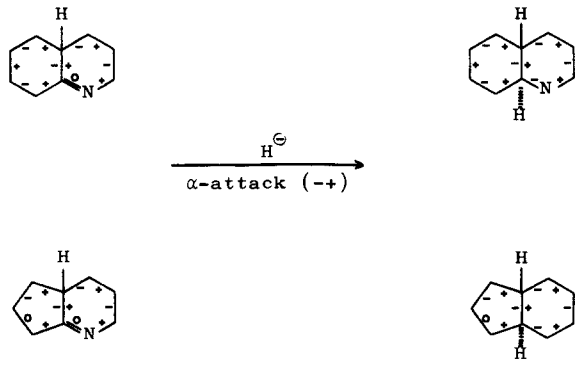
Very little has been reported on reduction of thioamides with complex metalhydrides (on $NaBH_4$ reduction of thioamides[36]). The reaction of thiolactams **10** with LAH under the same conditions as the lactams **2**, proceeded at a higher rate than the corresponding lactam reduction, and the yields of both the imine **11** and the acetylated compound **14** were slightly higher.

The imines **11** have been further reduced with LAH to the saturated amines, **15**. As expected using the torsion angle notation and the principle of least torsional distortion[37] on hydride reduction of the bicyclic imines, **11**, *trans*-decahydroquinoline and *trans*-octahydro-1(1 H)-pyridine[38] were isolated as main products.

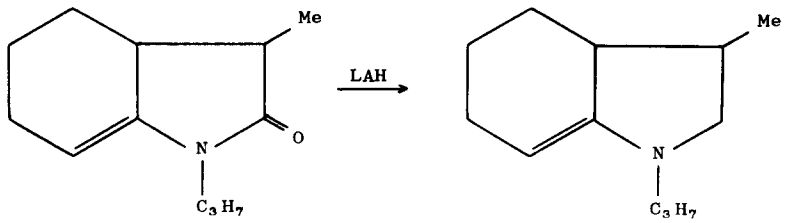
Reduction of the N-substituted lactam **6.1a** under the same conditions as **2** and **10** afforded the enamine **16**. No isomerisation or reduction of the double bond of **16** was observed.

EXPERIMENTAL

^{1}H NMR spectra were recorded at 60 MHz on a Varian A-60 spectrometer ($CDCl_3$) and the ^{13}C NMR spectra at 20 MHz on a CFT-20 Varian instrument ($CDCl_3$). TMS was used as internal

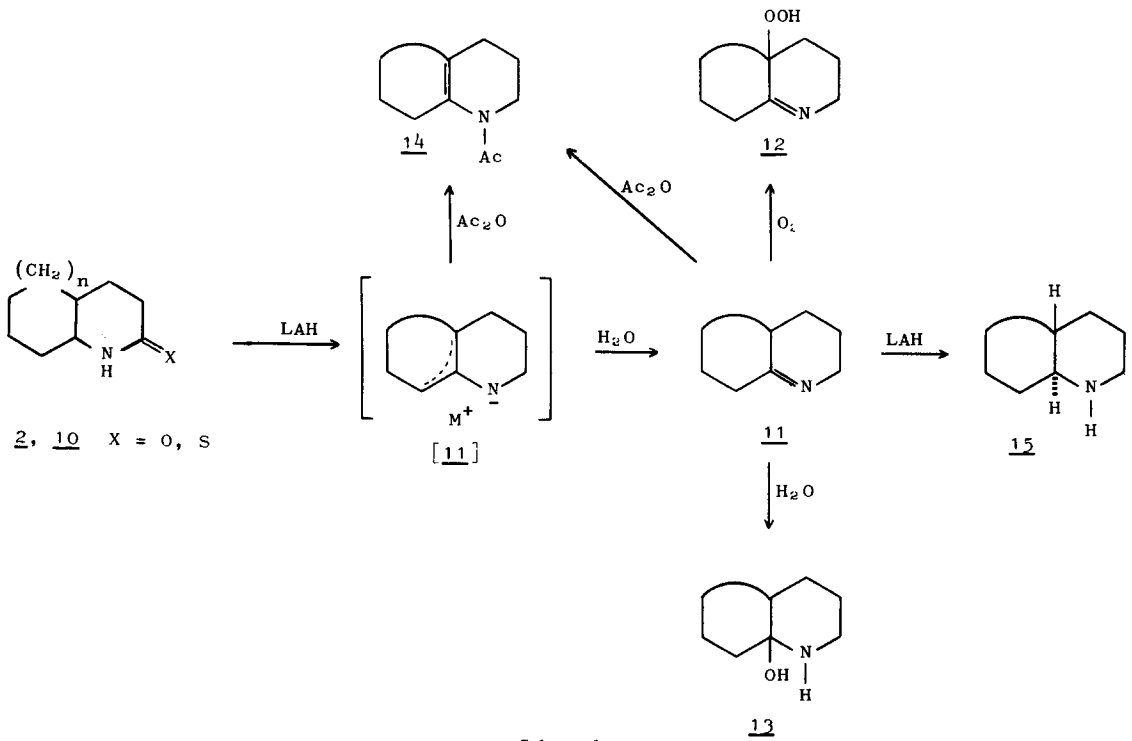


Scheme 4.



6, 1a 16

Scheme 5.



Scheme 6.

standard. Chemical shifts are expressed in δ-values. IR spectra were recorded on a Beckman IR-18 spectrometer. Mass spectra were recorded on a Micromass 7070 mass spectrometer operating at 70 CV using direct inlet. Precise measurements were performed at the chemical institute, Odense University, DK-5230 Odense M, on a Varian MAT 311A supervised by Prof. J. Møller. Glc analyses were carried out on a Hewlett Packard 5700A gas chromatograph equipped with a flame ionization detector, using SE 30 DMCS glass and 10% PEG 20 m, 1% KOH colums. Silica gel 60 (Merck) was used for column chromatography. M.ps and b.ps are uncorrected. Elementary analyses were carried out by LØVEN Microanalytical Laboratory, LØVEN Chemical Factory, DK-2750 BALLERUP.

Starting materials. The enamines 1, 3, and 5 were prepared

according to the literature.[2,6-8] The 2 - bromo - carboxamides (2 - bromo - N - cyclohexyl - acetamide and 2 - bromo - acetanilide) were prepared by known methods.[39] LR (now available from Fluka AG, CH-9470 Buch SG, and Aldrich 22743-9) was prepared as described.[14]

Reaction of **1** *with acrylamide* (**1**→**2**). 0.1 mole of acrylamide was added to a stirred soln of **1** (0.1 mol) in 50 ml anhyd. solvent (Table 1). The mixture was refluxed for 3 hr. The solvent was evaporated and **2** was purified by distillation under reduced pressure or by crystallisation from benzene–light petroleum. For small quantities purification may be performed on a column (silica gel, ether; $R_F \sim 0.3$).

General procedure for reaction with primary amines (**3**→**4**, **5**→**6**+**7** and **1**→**9**). A mixture of 0.01 mole of **1**, **3**, or **5** and 0.01 mole of the primary amine in 30 ml anhyd. solvent was stirred at elevated temp (Table 2) for 10–20 hr. After evaporation of the solvent, **4** and **6** were purified on a column (silica gel, ether). The imines **7** and **9** were purified by distillation under reduced pressure.

Ethyl 2 - *Benzylimino* - *cyclopentane* - 1 - *acetate* (**7**). Solvent: dioxane; reaction time 20 hr; yield 59%. b.p. 120°/0.2. MS (rel. int. %): 259 (M^+, 21), 214 (7), 186 (21), 172 (21), 125 (21), 91 (100). ^{1}H NMR (δ): 7.19 (s, 5 H, Ph), 4.4 (s, 2 H, CH_2N), 4.1 (q, J = 7 Hz, 2 H, OEt), 1.2 (t, J = 7 Hz, 3 H, OEt). ^{13}C NMR (δ): 180.2 (C=N), 173.0 (COOEt), 140.6 (C1-Ph), 128.2 (C2 or C3-Ph), 127.5 (C2 or C3-Ph), 126.4 (C4-Ph), 60.1 (OCH_2), 56.9 (CH_2N), 43.4, 36.7, 31.0, 29.2, 22.6, 14.2.

Cyclopentanone-benzylimine (**9**). Solvent: dioxane; reaction time 12 hr; yield 60%; b.p. 110°/0.5. ^{1}H NMR (δ): 7.3 (s, 5 H, Ph), 4.4 (s, 2 H, CH_2N), 2.0–2.5 (m, 4 H), 1.6–1.9 (m, 4 H). ^{13}C NMR (δ): 180.2 (C=N), 139.8 (C1–Ph), 127.6 and 127.2 (C2 and C3-Ph), 125.8 (C4-Ph), 57.0 (CH_2N), 35.9, 28.5, 24.4, 23.6. Cyclohexanone–benzylimine. Yield 97% B.p. 120°/0.3. ^{1}H NMR (δ): 7.28 (s, 5 H, Ph), 4.50 (s, 2 H, CH_2N), 2.35 (m, 4 H), 1.65 (m, 6 H). ^{13}C NMR (δ): 173.1 (C=N), 140.6 (C1-Ph), 128.1 and 127.5 (C2 and C3-Ph), 126.2 (C4-Ph), 53.8 (CH_2N), 39.8, 28.8, 27.5, 26.7, 25.8.

Alkylation of the enamines **1** *with* 2-*bromoamides* (**1**→**8**). The 2-bromoamides (0.01 mole) was added to a stirred soln of **1** (0.01 mole) and 0.011 mole $N(Et)_3$ (0.11 mole) in 30 ml anhyd. benzene or toluene. Stirring (under N_2) was continued at room temp for 1–2 hr. The mixture was filtered, the solvent evaporated and **8** purified by column chromatography (SiO_2, ether).

2 - (1 - *Pyrrolidinyl*) - *acetanilide*. From 1 - (1 - pyrrolidinyl) cyclopentene and 2-bromoacetanilide: yield 58% (reaction temp 25°). From 1-(1-pyrrolidinyl) cyclohexene and 2-bromo-acetanilide: yield 85% (reaction temp 25°); yield 80% (reaction temp 80°). ^{1}H NMR (δ): 9.1 (s, 1 H, NH), 7.4 (m, 5 H, Ph), 3.2 (s, 2 H, CH_2CO). ^{13}C NMR (δ): 168.2 (C=O), 137.2 (C1-Ph), 128.7 (C2 or C3-Ph), 128.0 (C2 or C3-Ph), 123.1 (C4-Ph), 59.0 ($\underline{C}H_2CO$), 53.7 (2C), 23.3 (2C).

N - *Cyclohexyl* - 2 - (1 - *pyrrolidinyl*) - *acetamide*. From 1 - (1 - pyrrolidinyl) cyclohexene and 2 - bromo - N - cyclohexyl - acetamide: yield 90%; m.p. 70°; ^{1}H NMR (δ): 7.0 (s, 1 H, NH), 3.15 (s, 2 H, CH_2CO). ^{13}C NMR: 168.3 (C=O), 58.3 ($\underline{C}H_2$–CO), 53.3 (2C, CH_2N), 46.3, 31.9 (2C, $C\underline{H}_2N$), 23.8, 22.3, 24.5 (identical in all respects with an authentic sample).

General procedure for the thiation of **2** *and* **6** (**2**,**6** $\xrightarrow{LR}$ **10**). The starting compound (0.01 mole) and 2.02 g (0.005 mole) of LR were mixed in 10 ml anhyd. benzene at room temp with stirring until no more of the starting material could be detected (tlc). Then the mixture was concentrated and absorbed on silica gel under reduced pressure, and applied to silica gel column using ether/light petroleum as eluant. The conditions and the physical and spectroscopic data are summarized in Table 3.

General procedure for reduction of the lactams **2**, **4**, *and* **6**. To an ice-colled soln of LAH (0.1 mole) in anhyd. ether (50 ml, stirring, N_2) the lactam (0.05 mole) was added. Stirring was continued at room temp for 3 hr and 3.8 g H_2O added dropwise (5 min) at 0° followed by 2.85 g 30% NaOH + 28 g H_2O. The icebath was removed and stirring was continued for 15 min at room temp. The mixture was then filtered and extracted twice with ether. The combined ether extracts were dried ($MgSO_4$), concentrated and and **11** and **16**, purified by distillation under reduced pressure. (To avoid formation of peroxides the distillation was performed over solid KOH).

Reduction of the thiolactams, **10**. As above, reaction time 1 hr. Compound (n = 1) from **2a**: yield 79%. From **10a**: yield 87%; b.p. 70°/11; ^{1}H NMR (δ): 3.5 (m, 2 H), 1.7–2.6 (m, 13 H); ^{13}C NMR (δ): 173.3 (C=N), 49.6, 39.3, 38.7, 35.0, 28.0, 27.5, 26.0, 22.2. Compound **11** (n = 0) from **2d**: yield 69%. From **10'd**: yield 77%; b.p. 67–70°/12. ^{1}H NMR (δ): 3.5 (m, 1 H), 3.0 (m, 1 H), 1.7–2.7 (m, 11 H). ^{13}C NMR (δ): 179.2 (C=N). IR, film (cm^{-1}): 1675 (m). MS (rel. int. %): 123 (M^+, 54), 122 (65), 98 (100), 96 (79), 95 (63), 84 (17), 82 (22), 67 (35), 55 (26), 41 (30). Compound **13** (n = 1), m.p. 136°; ^{1}H NMR (δ, D_2O): 2.5–2.8 (m, 2 H, CH_2N). IR (KBr) cm^{-1}: 3300 (s), 3100 (s). MS (rel. int. %): 155 (M^+, 76), 138 (60), 137 (80), 126 (45), 122 (78), 99 (100), 96 (90), 84 (25), 82 (30), 70 (100). Compound **13** (n = 0), m.p. 127°; ^{1}H NMR (δ, D_2O): 2.8 (2, J = 5 Hz, 2 H, CH_2N). IR (KBr, cm^{-1}): 3300 (s), 3100 (s). MS (rel. int. %): 141 (M^+, 43), 124 (65), 123 (70), 112 (60), 99 (81), 96 (89), 84 (46), 70 (90), 56 (100). Compound **14**, yield 85%; ^{1}H NMR (δ): 4.4 (s, 1 H), 3.0–3.5 (m, 2 H), 1.0 (m, 6 H). MS (rel. int. %): 179 (M^+, 46), 164 (100), 150 (62), 136 (36), 122 (23), 94 (8), 67 (8), 41 (13). Precise measurement on M^+ (Calc. for $C_{12}H_{21}N$: 179.1642, found 179.1665).

Reductive acetylation of lactams, and thiolactams (**2**, **10**→**14**). Same procedure as above until decomposition of the mixture. Then at −15°, 25 ml Ac_2O were added (3 min). Immediately afterwards the mixture was decomposed in the normal manner by dil. NaOH aq. The acetylated compounds **14** were then purified by distillation or by column chromatography (silica gel, ether, $R_F \sim 0.5$). Compound **14** (n = 0), from **2d**: yield 54%. From **10'd**: yield 62%; ^{1}H NMR (δ): 3.5 (m, 1 H, CH_2N), 2.9 (m, 1 H, CH_2N), 2.18 (s, 3 H, Ac). MS (rel. int. %): 165 (M^+, 66), 137 (41), 122 (100), 95 (40), 43 (99). Compound **14** (n = 1), from **2a**: yield 39%. From **10'a**: yield 58%; ^{1}H NMR (δ): 3.52 (t, J = 5.5 Hz, 2 H, CH_2N), 2.11 (s, Ac). ^{13}C NMR (δ): 169.7 (C=O), 133.1, 106.4. MS (rel. int. %): 179 (M^+, 79), 137 (100), 136 (82), 109 (84), 43 (25). Precise measurements on M^+ (Calc. for $C_{11}H_{17}NO$, 179.1309, found 179.1300).

Acetylation of imines (**11**→**14**). To a soln of 0.005 mol $\Delta^{1(8a)}$-octahydroquinoline and 0.005 mol NEt_3 in 10 ml ether 1 ml Ac_2O was added and stirred 0.5 hr at room temp. The soln was filtered, concentrated under reduced pressure and purified as above, yield 90%.

Reduction of the imines **11**→**15**. Same procedure as the lactam reduction but with equimolar amounts of LAH and imine, reaction time 2 hr. The saturated amines, **15**, were purified by distillation under reduced pressure or by crystallisation from ether–light petroleum. Compound **15** (n = 0), yield 90%, *trans*:*cis* = 93 : 7 (glc). Compound **15** (n = 1), yield 86%, *trans*:*cis* = 96 : 4 (glc). Spectroscopic and physical data of **15** are in agreement with earlier reports.[38,40-42]

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