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SYNTHESIS OF NEW α-CHLOROACRYL-AMIDES, THIOAMIDES AND AMIDINES FROM SATURATED AMIDES

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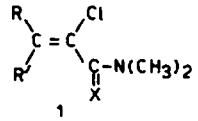
Abstract *Chorination of saturated amide-chlorides followed by hydrolysis thiolysis, aminolysis and catalysed dehydrochlorination leads to α-chloro acrylamide derivatives in high yield The reaction sequence is applied to lactames and can also be extended to the synthesis of α-chloro acrylthioamide and amidine*

Our continuing interest in double or triple bond activation by polar substituents[1] is centered in this publication on the synthesis of α-chloroacrylamides **1a**, thioamides **1b** and amidines **1c**, which are mostly new and promise many applications for hetero and homocyclisations and for other additions reactions which will be reported in following papers [2,3]



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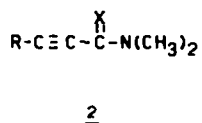
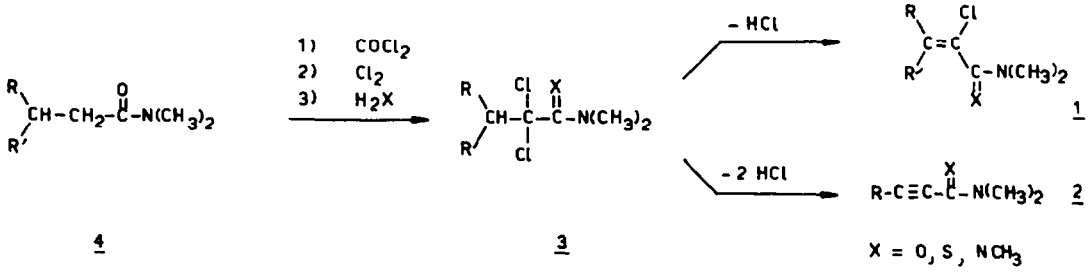


2

a) X = O
b) X = S
c) X = NCH$_3$

Our approach to acrylic compounds **1**, and also to alkynes **2**, is based on a catalytic dehydrochlorination of the α-dichloro-amide derivatives **3**, which in turn can be obtained from saturated amides **4**



4 **3** **1** **2**

The first reaction step constitutes the already described chlorination of the amide chlorides **5** (in equilibrium with the α-chloro-enamines **6**[4]) The salts **7** are not isolated and their hydrolysis gives the dichloroamides **8** as exemplified in Table I

Scheme 1

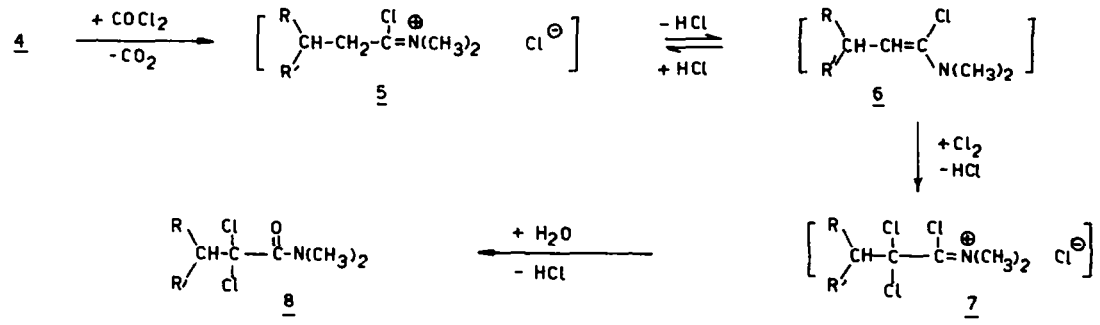


Table I Synthesis of α-dichloro-amides 8

Compound	R	R'	Yield of 8 (%)	Ref
a	H	H	62-72	4
b	CH_3	H	62	4
c	CH_3	CH_3	78	this work
d	$nC_{13}H_{27}$	H	56	this work

Whereas hydrochloric acid elimination by bases is not satisfactory[5], the reaction of **8** with two equivalents of technical grade aluminium chloride in refluxing dichloromethane affords the acrylic derivatives **9** and **10** in good yields (Table II) These compounds are stable and are purified by distillation, except in the case of **9d**, which is isolated by column chromatography[6]

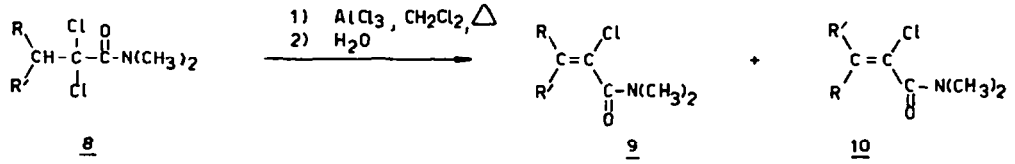
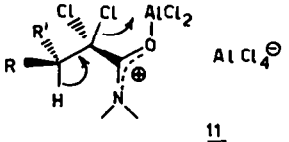


Table II Synthesis of α-chloro-acryl-amides **9** and **10**

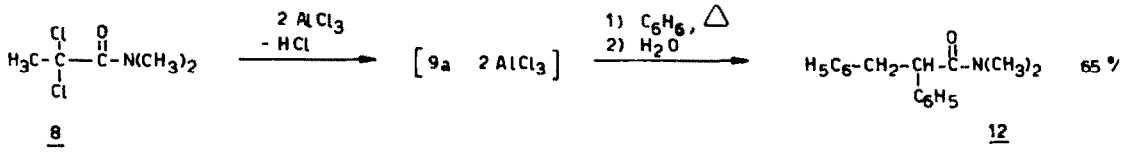
Compound	R	R'	Yield of 9+10 (%)	9 10
a	H	H	84	-
b	CH_3	H	82	96 4
c	CH_3	CH_3	73	-
d	$nC_{13}H_{27}$	H	78	100 0

This elimination proceeds with high stereoselectivity (as exemplified by **8b** and **8d**) The use of only one equivalent of aluminium chloride results in a lowering of the reaction rate and yield This dependance on the amount of Lewis acid can be explained by the formation of a complex salt **11** as a prerequisite to induce elimination of hydrochloric acid



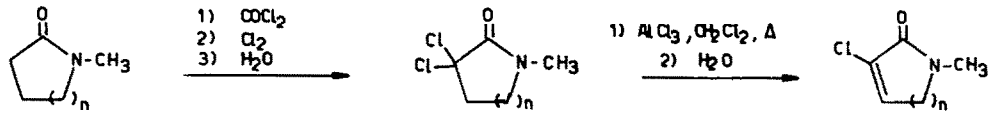
The reaction time varies from 24 to 48 hours, depending on the grade of aluminium chloride which is neither purified nor ground before use The synthesis of **9a** can be run on a 100 gr scale

The use of benzene as solvent with **8a** leads to the formation of the diphenyl propionamide **12** in the isolated yield of 65 %, by successive elimination and double arylation of **9a**



8 **12**

The sequence described in scheme I can also be applied to cyclic N-methylated amides **13**, leading to their dichloro derivatives **14** and to the new unsaturated lactames **15** in excellent yields (Table III)

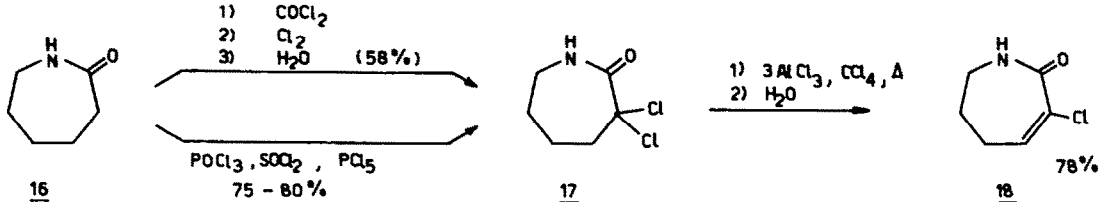


13 **14** **15**

Table III Synthesis of the α-dichloro-lactames **14** and α-chloro-α,β-dehydro-lactames **15**

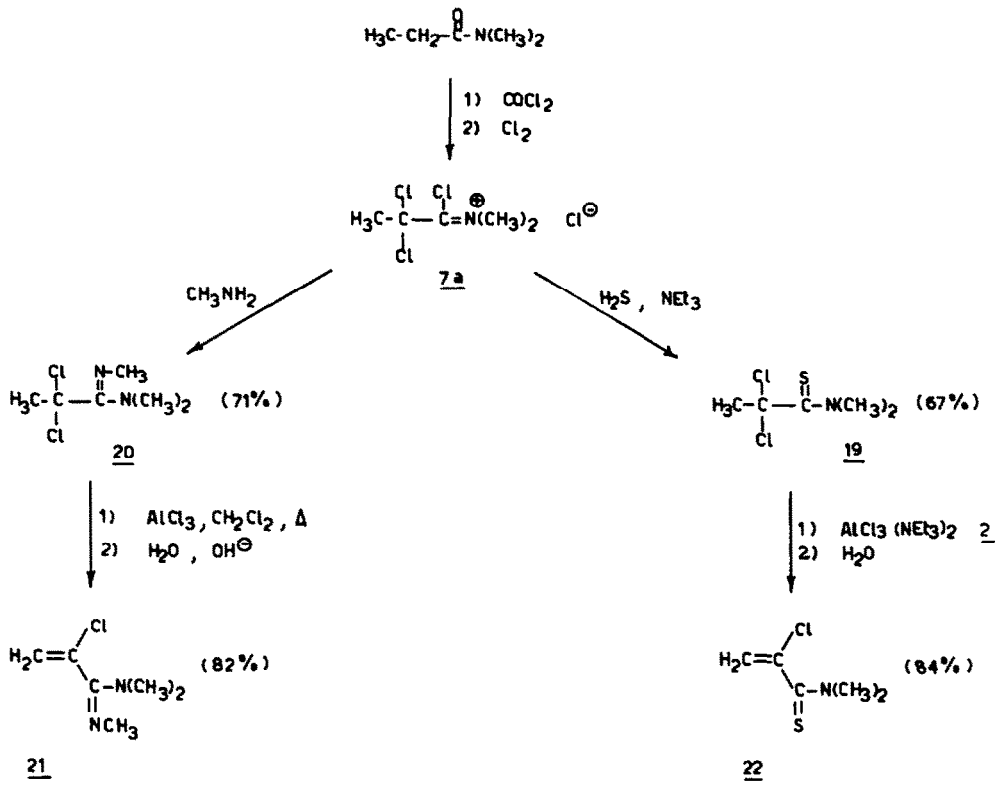
Compound	n	14 %	15 %
a	1	40 (lit [4] 48)	[93] [7]
b	2	74	95
c	3	70	94

Analogously, caprolactame itself can be chlorinated to give the α-dichloro derivative **17**, either by the use of phosgene and chlorine, or by treatment with a mixture of $POCl_3$, $SOCl_2$ and PCl_5 [8] In the case of this secondary amide **17**, the elimination reaction needs 3 equivalents of Lewis acid and higher temperature (refluxing tetrachloromethane), giving **18** in 78 % yield [5]



16 **17** **18**

The salt **6a** (R,R'=H) can also be thiolysed with hydrogen sulfide or aminolysed with methylamine These two reactions lead to the thioamide **19** and amidine **20** in 67 and 71 % yield respectively In the presence of aluminium chloride and in refluxing dichloromethane, compound **20** is transformed into the expected 2-chloro-propenamide **21** in 82 % yield In the case of **19**, the modified reagent **23** [9] is necessary to perform elimination of HCl, the ensuing aqueous work-up leads to the new acrylic thioamide **22** with 84 % yield



Despite modification of work-up procedures, the use of "free" aluminium chloride to perform the reaction step **19** to **22** leads always to a mixture of **22** and **9a**, but when the complex **23** is used, no amide **9a** is detected The absence of **9a** is probably due to a weaken ng of the thioamide complex during hydrolysis

The reactions described in this paper permit an efficient synthesis of the new or little known acrylic monomers[10] whose potential is being explored in our group Furthermore, if aluminium chloride is widely used in Friedel-Crafts type reactions and for rearrangements of carbon skeletons[11], its efficiency for dehydrohalogenation reactions is much less documented[12] The use of cheap reagents like phosgene, chlorine and aluminium chloride, under mild conditions, represents a very useful method for derivatisations of saturated amides

Experimental Part

Boiling points are uncorrected, melting points were mesured on a Leitz Wetzlar HM Lux and are uncorrected ^{1}H-NMR spectra were recorded in $CDCl_3$ solution using TMS as internal reference at 200 MHz on Varian XL-200 spectrometer or at 60 MHz on Varian EM-360 (s=singulet, d=doublet, t=triplet, m=multiplet, J=coupling constant in Hz) Infrared spectra were recorded on a Perkin-Elmer 297 infrared spectrometer Mass spectra were recorded on Varian Mat-44S spectrometer and are given for the 35 chlorine isotope (under brackets for other isotopes) Microanalyses were performed by the microanalyses Laboratory of the University of Wien

N,N-dimethyl 2,2-dichloro propanamide 8a[4]

101 grs (1 mole) of phosgene are added to a cold (-78°C) solution of 101 grs (1 mole) of N,N-dimethyl propanamide in 200 ml of dichloromethane The temperature is then slowly raised and kept at 20°C until the end of evolution of CO_2 ($\sim$ 1 hour). The mixture is then saturated with chlorine when keeping the temperature below 30°C by use of an ice-bath After standing during 12 hours, the mixture is hydrolysed by careful addition of 200 ml of water After neutralization by sodium carbonate, the dichloroamide in extracted with dichloromethane, dried on sodium sulfate and distilled at 80°C/17 Torr (yield = 105 to 124 grs, 62 to 74%) IR (neat) ν = 2950, 1640, 1370, 1080 cm^{-1} NMR ($CDCl_3$) δ = 2 33(3H,s), 3 20(6H,s) ppm MS(m/e) = 169 (173), 135(137), 120, 100

N,N-dimethyl 2,2-dichloro butanamide 8b[4]

Same procedure as for **8a** 105 grs (0 91 mole) of N,N-butanamide give, after distillation at 98°C/17 Torr , 103 5 grs (62%) of **8b** as a colourless liquid IR (neat) ν = 2940, 1640, 1380, 1060 cm^{-1} NMR ($CDCl_3$) δ = 1 20(3H,t), 2 70(2H,q), 3 30(6H,s) ppm MS(m/e) = 182(185), 148, 113

N,N-dimethyl 2,2-dichloro 3-methyl butanamide 8c

Same procedure as for **8a** 11 4 grs (0 1 mole) of NN dimethyl 3 methyl butanamide give 15 6 grs (78%) of **8c** Bp 115°C/17 Torr IR (neat) ν = 2940, 1630, 1380, 700 cm^{-1} NMR ($CDCl_3$) δ = 1 18(6H,d, J = 6 Hz), 2 96(1H,m, J = 6Hz), 3 20(6H,s) ppm MS(m/e) = 197(199, 201), 162(164), 127, 118(120)

N,N-dimethyl 2,2-dichloro hexadecanamide 8d

Same procedure as for **8a** 19 7 grs (0 07 mole) of N,N-dimethyl palmitic amide lead to 13 8 grs (56%) of **8d** purified by column chromatography (silica, benzene, Rf = 0 7) IR (neat) ν = 2920, 1640, 1385, 1050 cm^{-1} RMN ($CDCl_3$) δ = 1 1-1 9(27H,m), 2 4(2H,t), 3 1(6H,s) ppm MS(m/e) = 351 (353, 355), 316(318), 177, 154(156)

N-methyl 3,3-dichloro pyrrolidone 14a[4]

Same procedure as for **8a** 4 9 grs of **13a** afford 3 27 grs (40 %) of **4a** (lit[4] 48%) B p 130°C/17 Torr M p 40°C (lit[4] 42°C) IR (CH_2Cl_2) ν = 2950, 1710, 1290, 840 cm^{-1} NMR ($CDCl_3$) δ = 2 86(2H,t, J = 5 8Hz), 2 95(3H,s), 3 45(2H,t, J = 5 8Hz)ppm $C_7H_5Cl_2NO$ (162 03) found (calc) C 36 00(35 74), H = 4 55(4 20), Cl = 41 99(42 20), N = 8 42 (8 34)

N-methyl 3,3-dichloro piperidone 14b

Same procedure as for **8a** 12 grs of **13b** (0 106 moles) furnish, after crystallization from diisopropylether, 14 22 grs (74%) of **14b** as white crystals (m p 81 5°C) IR (CH_2Cl_2) ν = 2950, 1655, 1195, 805 cm^{-1} NMR ($CDCl_3$) δ = 2 11(2H,m), 2 77(2H,m), 2 97(3H,s), 3 88(2H,t, J = 5 6 Hz)ppm MS(m/e) = 181(183, 185), 146(148), 118(120), 96, 72 $C_6H_9Cl_2NO$ (182 06) found (calc) C 39 87(39 58), H 5 11(4 98), Cl 38 81(38 95), N 7 83(7 69)

N-methyl 3,3-dichloro caprolactame 14c

Same procedure as for **8a** 8 85 grs (0 07 mole) of **13c** give, after purification on column chromatography (alumina, C_6H_6/AcOEt 3/7), 9 5 grs (70%) of **14c** as colorless oil (m p ∿ 15°C) IR (CH_2Cl_2) ν = 2950, 1640, 1390, 1170, 980 cm^{-1} NMR ($CDCl_3$) δ = 1 85(4H,m), 2 56(3H,m), 3 05 (3H,s), 3 55(2H,m)ppm MS(m/e) = 195(197, 199), 160(162), 132(134), 96

α-dichloro caprolactame 17

Same procedure as for **8a** 113 grs (1 mole) of caprolactame **16** furnish, after crystallization from methanol, 105 grs (58%) of **17** as white crystals M p 126°C (lit[7] 124-126°C) IR (CH_2Cl_2) ν = 3400, 3250, 2950, 1660, 1260, 890 cm^{-1} NMR ($CDCl_3$) δ = 1 4-2 3(4H,m), 2 63(2H,m), 3 43(2H,m), 7 65(1H,N-H)ppm MS(m/e) = 181(183, 185), 146(148), 111, 96 $C_6H_9Cl_2NO$ (182 06) found (calc) C 39 85(39 58), H 5 05(4 98), Cl 38 87(38 95), N 7 91(7 69)

N,N-dimetnyl 2,2-dichloro propanethioamide 19

50 5 grs (0 5 mole) of phosgene are added to 50 5 grs (0 5 mole) of N,N-dimethylpropanamide dissolved in 100 ml of dichloromethane at -78°C The temperature is then slowly raised and kept at 20°C until end of evolution of CO_2 (∿ 1 hour) The mixture is then saturated by chlorine, when keeping the temperature below 30° by use of ice-bath After standing for 12 hours, the excess chlorine and the formed HCl are removed by passing a stream of nitrogen into the reaction mixture The solution is then saturated with H_2S and 75 grs (0 75 mole) of NEt_3 are added Stirring is maintained during 6 hours The mixture is poured into 300 mls of water and the thioamide is extracted by dichloromethane, dried on sodium sulfate and distilled at 74°C/0 4 Torr Yield 61 5 grs (67%) Yellow liquid which crystallizes slowly (m p 30°C) IR (CH_2Cl_2) ν = 2950, 1380, 1060, 920 cm^{-1} NMR ($CDCl_3$) δ = 2 59(3H,s), 3 47(3H,s), 4 55(3H,s) ppm MS(m/e) = 185(187, 189), 150(152), 115, 100, 88

N,N,N'-trimethyl 2,2-dichloro propaneamidine 20

The amide chloride **6a** is prepared from 50 5 grs (0 5 mole) of N,N-dimethyl propanamide as for **19** After standing during 12 hours and elimination of the excess of Cl_2 and HCl, the reaction mixture is aminolyzed by gazeous methylamine and poured into aqueous sodium hydroxide solution After extraction by dichloromethane, drying on sodium carbonate and evaporation of solvent, **20** is distilled at 81°C/17 Torr Yield 64 6grs (71%) IR (neat) ν = 2930, 1620, 1440, 1340, 1050 cm^{-1} NMR ($CDCl_3$) δ = 2 37(3H,s), 2 97(6H,s), 3 15(3H,s)ppm MS(m/e) = 182(184, 186),

157(159), 132(134), 106(108), 103(105), 85

N,N-dimethyl 2-chloro propenamide 9a

119 grs (0 7 mole) of a solution of **8a** in 100 ml of dichloromethane is added dropwise to 200 grs (1 5 mole) of aluminium chloride in 300 ml of dichloromethane The mixture is refluxed until end of evolution of HCl After cooling, the dark solution is poured into a cold solution of 180 grs (4 5 moles) of sodium hydroxide in 500 ml of water 60 grs of ammonium chloride are then added and the aluminium salts are filtered through celite The filtrate is decanted and the aqueous layer is extracted by dichloromethane The combined organic phases are dried over sodium sulfate and evaporated The amide **9a** is then distilled at 78°C/17 Torr as a colorless liquid Yield 87 grs (93%) IR (neat) ν = 3050, 2990, 1640, 1400 cm^{-1} NMR ($CDCl_3$) δ = 3 03 (6H, s), 5 61(1H,d, J = 2Hz), 5 63(1H,d, J = 2Hz)ppm MS(m/e) = 133(135), 118(120), 81(83)

N,N-dimethyl 2-chloro-butenamides 9b and 10b

Same procedure as for **9a** 91 5 grs (0 5 mole) of **8b** furnish 60 3 grs (82%) of a 96 4 mixture of **9b** and **10b** (determined by gas chromatography) B p 100°C/17 Torr (colorless liquid) IR (neat) ν = 3070, 2980, 1620, 1400 cm^{-1} NMR (for **9b**)($CDCl_3$) δ = 1 84(3H,d, J = 6 7 Hz), 2 97(6H,s), 5 95(1H,q, J = 6 7 Hz)ppm MS(m/e) 147(149), 132(135), 103

N,N-dimethyl 2-chloro-3-methyl butenamide 9c

Same procedure as for **9a** 4 grs of **8c** yield 2 35 grs (73%) of **9c** as a colorless liquid boiling at 130°C/17 Torr IR (neat) ν = 3050, 2990, 1620, 1300 cm^{-1} NMR ($CDCl_3$) δ = 1 78(2H,s), 1 87(3H,s), 3 02(6H,d)ppm MS(m/e) 161(163), 146(148), 131, 116

N,N-dimethyl 2-chloro hexadecenamide 9d

Same procedure as for **9a** 6 grs of **8d** give, after purification by column chromatography over alumina (eluent chloroform), 4 18 grs (78%) of **9d** as a yellowish oil IR (CH_2Cl_2) ν = 3070, 2970, 1620, 1410 cm^{-1} NMR ($CDCl_3$) δ = 0 9-2 23(27H,m), 3 02(6H,s), 5 97(1H,t, J = 7 Hz)ppm MS(m/e) 315(319), 300(302), 280, 271(273)

N-methyl 3-chloro-3,4-dehydropyrrolidone 15a

Same procedure as for **9a** 2 grs of **14a** afford 2 44 grs (93%) of **15a** which is rather unstable and could not be purified neither by distillation nor by crystallization M p 30°C (dec) IR (CH_2Cl_2) ν = 3050, 2940, 1690, 1380, 1240 cm^{-1} NMR ($CDCl_3$) δ= 3 10(3H,s), 4 02(2H,d, J = 1 9 Hz), 7 0(1H,t, J = 1 9 Hz)ppm SM(m/e) 131(133), 116(117), 88(70)

N-methyl 3-chloro-3,4-dehydropiperidone 15b

Same procedure as for **9a** 10 grs (0 05 mole) of **14b** furnish, after Kugelrohr distillation at 93°C/0 02 Torr , 7 58 grs (95%) of a colourless liquid which slowly crystallizes IR (CH_2Cl_2) ν = 3050, 2940, 1650, 1605, 1375 cm^{-1} NMR ($CDCl_3$) δ = 2 47(2H,td, J_t = 7 2 Hz, J_d = 4 6 Hz), 3 00 (3H,s), 3 45(2H,t, J = 7 2Hz), 6 63 (1H,t, J = 4 6Hz)ppm C_6H_8ClNO (145 59) found (calc) C = 49 78(49 50), H 5 49(5 54), Cl 24 15(24 35), N = 9 71(9 62)

N-methyl 3-chloro-3,4-dehydrocaprolactame 15c

Same procedure as for **9a** 5 07 grs (0 026 mole) of **14c** furnish, after Kugelrohr distillation at 98°C/0 03 Torr, 3 89 grs (94%) of **15a** as a colourless liquid which slowly crystallizes on cooling IR (CH_2Cl_2) ν = 3050, 2940, 1660, 1605, 1430 cm^{-1} NMR ($CDCl_3$) δ = 1 73-2 43(4H,m), 3 05(3H,s), 3 85(2H,t, J = 5 5 Hz), 6 37(1H,t, J= 7 Hz) ppm MS(m/e) 159(161), 124(126), 106, 84 $C_7H_{10}ClNO$ (159 62) found (calc) C 52 85 (52 67), H 6 31(6 31), N 8 84(8 78)

3-chloro-3,4-dehydrocaprolactame 18

90 5 grs (0 5 mole) of **17** dissolved in a minimum amount of warm dichloromethane are added to 220 grs (1 6 mole) of aluminium chloride in 300 mls of carbon tetrachloride The mixture is then refluxed until end of evolution of HCl (~ 20 hours) After cooling, the dark solution is poured into a solution of 180 grs (4 5 moles) of sodium hydroxide in 500 mls of ice cold water, 60 grs of ammonium chloride are added and the precipitate is filtered trough celite The filtrate is extracted by dichloromethane After drying over sodium sulfate and evaporation of solvent, the resulting solid is recrystallized from methanol to give 56 6 grs (78%) of **18** as a white solid (m p 83°C) IR (CH_2Cl_2) ν = 3410, 3220, 3050, 2980, 1630, 1605, 1410 cm^{-1} NMR ($CDCl_3$) δ = 1 95(2H,m), 2 28(2H,m), 3 05(2H,m), 6 52(1H,t, J= 6 4Hz), 8 12(1H, N-H) ppm MS(m/e) = 145(147, 149), 116(117), 102(104), 88, 70 C_6H_8ClNO (145 59) found (calc) C 49 53(49 50), H 5 11(5 54), Cl 24 19(24 35), N 9 72 (9 62)

N,N-dimethyl 2,3-diphenyl propanamide 12

A solution of 8 5 grs (0 05 mole) of **8a** in 10 mls of benzene is added to a suspension of 16 grs (0 12 mole) of aluminium chloride in 40 ml of benzene The mixture is then refluxed during 40 hours and, after cooling, poured into a cold solution of 14 4 grs of sodium hydroxide in 80 ml of water 6 grs of ammonium chloride are added and the precipitate is filtered on celite The filtrate is decanted and the aqueous layer is extracted by dichloromethane The combined organic phases are dried on sodium sulfate and evaporated The residue is recrystallized from cyclohexane giving 8 22 grs (65%) of **12** as white crystals (m p 85 5°C) IR (CH_2Cl_2) ν = 3060, 2930, 1630, 1600, 1400 cm^{-1} NMR ($CDCl_3$) δ = 2 7(3H,s), 2 8(3H,s), 2 91(1H,dd, ^3J = 7 03 Hz, ^2J = 13 4 Hz), 3 46 (1H,dd, ^3J = 7 98 Hz, ^2J = 13 4 Hz), 3 4(1H,dd, ^3J = 7 98 Hz, ^3J = 7 03 Hz), 7 15(10H,m) ppm MS(m/e) = 253, 238, 223, 207, 181, 162, 72

N,N,N'-trimethyl 2-chloropropenamidine 21

Same procedure as for **9a** (The crude **21** is extracted with dichloromethane from the strongly alcaline solution) 25 grs (0 137 mole) of **20** give, after distillation at 63°C/17 Torr, 16 5 grs (82%) of **21** as a colourless liquid IR (neat) ν = 3050, 2950, 1680, 1605, 1480 cm^{-1} NMR ($CDCl_3$) δ = 2 88(6H,s), 3 07(3H,s), 5 32(1H,d, J= 1 8 Hz), 5 70(1H,d, J = 1 8 Hz) ppm MS(m/e) = 146(148), 111, 102(104), 85

N,N-dimethyl 2-chloropropenethioamide 22

86 8 grs (0 88 mole) of triethylamine are added to a suspension of 57 2 grs (0 44 mole) of aluminium chloride in 400 ml of dichloromethane After stirring during 1 hour at room temperature, 40 grs (0 22 mole) of **19** are added The mixture is refluxed until disappearance of the starting material (∿ 10 hours, monitoring by TLC on silicagel, eluent CH_2Cl_2) The dark solution is then poured into 250 ml of ice cooled water Extraction by dichloromethane, followed by drying on sodium sulfate and evaporation leads to a dark liquid which is distilled at 53°C/0 03 Torr to give 27 1 grs (84%) of **22** as a yellow liquid which must be kept at 0°C IR (CH_2Cl_2) ν = 3050, 2980, 1620, 1500, 1385 cm^{-1} NMR ($CDCl_3$) δ = 3 34(3H,s), 3 40(3H,s), 5 38(1H,d, J = 2 2 Hz), 5 48(1H,d, J = 2 2 Hz) ppm MS(m/e) = 147(151), 134(136), 105(107), 61

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