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N-ALKOXY-N-ACYLNITRENIUM IONS IN INTRAMOLECULAR AROMATIC ADDITION REACTIONS

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Abstract - N-alkoxy-N-acylnitrenium ions are generated by treatment of N-alkoxy-N-chloroamides with silver ions in ethereal solvents. These intermediates readily cyclise onto aromatic nuclei on alkoxy side-chains to give benzoxazines and benzoxazepines and on the acyl side-chains to give γ, δ and ε benzolactams. Spirane products are formed by ipso addition when a 4-methoxy substituent is present on the side-chain aromatic rings. The yields and regioselectivities of these reactions have been ascribed to different transition structures for cyclisation onto the acyl and alkoxy side-chains which involve respectively an exocyclic and endocyclic $\overset{\oplus}{N}$-O π-bond. Evidence for this exeptionally high π-bond character has been obtained from MNDO calculations which predict a π-bond order of 0.9 and a rotational barrier of 29.7 kcalmol^{-1}

INTRODUCTION

Recently we reported that N-chloro-N-alkoxyamides (2) undergo intramolecular and intermolecular aromatic substitution through the intermediacy of N-acyl-N-alkoxynitrenium ions which were generated in benzene by treatment of (2) with silver or mercury salts.[1] (reaction 1)

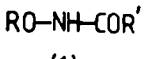
$$Ag^{+} + RO\text{-}NCl\text{-}COR' \longrightarrow AgCl + RO\text{-}\overset{+}{N}\text{-}COR' \quad \ldots\ldots 1$$

The facility with which this occurred was demonstrated in the synthesis of two novel fused heterocycles, the 2,1-benzoxazines (4) and (5) and the 2,1-benzoxazepine (6). Concurrent with this work, Kikugawa and Kawase reported similar cyclisations onto the acyl side-chain of the N-chlorohydroxamic esters (2) to give good yields of N-methoxylactams.[2] Their conditions involved silver carbonate induced heterolysis of the nitrogen-chlorine bond in trifluoroacetic acid. We now report that the same cyclisation can be effected under our milder conditions which, in addition, we have optimised. Furthermore we have established that when a 4-methoxyaryl substituent is present upon the recipient ring on either side-chain, the dominant mode of cylisation is not Ar_2-n but rather Ar_1-n. In these cases spiro-fused bicyclic structures (18)-(22) are formed. Competition reactions have been carried out to establish the regioselectivity of the cyclisations and intermolecular addition has been observed with both benzene and toluene as solvent.

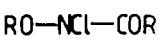
RESULTS

Our initial cyclisations involved the use of silver or mercury salts as Lewis acids in benzene as solvent.[1] However table 1 shows that the formation of 2,1-benzoxazines (4) and (5) is best effected with silver salts in ethereal solvents. Near quantitative conversion was obtained with $AgBF_4$ in anhydrous T.H.F. or diethyl ether. Under these conditions the 2,1-benzoxazepine (6) was formed in an improved yield of 50%. However O-benzyl-N-chlorobenzohydroxamate (2a) could not be cyclised to (3) under our conditions or in trifluoroacetic acid with Ag_2CO_3[2] (table 2).

The yields of N-methoxybenzolactams (11)-(13) formed from the methyl-N-chloro-ω-phenylalkanohydroxamates (21)-(2n) are given in table 2. The yields of (12) and (13) compare favourably with those obtained in trifluoroacetic acid by Kikugawa and Kawase.[2] Our cyclisations were however accompanied by competitive intermolecular aromatic substitutions when benzene was used as a co-solvent. Only (12) could be analysed as a solid however all three benzolactams (11), (12) and (13) gave characteristic carbonyl absorptions in their infrared spectra and a common $[M-59]^{+}$ fragment in their mass spectra. This could arise by sequential McLafferty rearrangement (loss of formaldehyde), decarbonylation and deprotonation (scheme 1, R=H). Such fragmentation appears to be characteristic of fused N-alkoxylactams.



(1)



(2)

(a) R = $-CH_2Ph$, R' = Ph

(b) R = $-(CH_2)_2Ph$, R' = Ph

(c) R = $-(CH_2)_3Ph$, R' = Ph

(d) R = $-(CH_2)_2Ph$, R' = CH_3

(e) R = $-(CH_2)_2$(4-MeOPh), R' = Ph

(f) R = $-(CH_2)_3$-(4-MeOPh), R' = Ph

(g) R = $-(CH_2)_2Ph$, R' = $-(CH_2)_2Ph$

(h) R = $-(CH_2)_2Ph$, R' = $-(CH_2)_3Ph$

(i) R = $-(CH_2)_3Ph$, R' = $-(CH_2)_2Ph$

(j) R = $-(CH_2)_3Ph$, R' = $-(CH_2)_3Ph$

(k) R = Me, R' = Ph

(l) R = Me, R' = CH_2 Ph

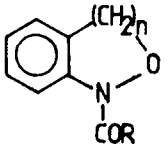
(m) R = Me, R' = $(CH_2)_2Ph$

(n) R = Me, R' = $(CH_2)_3Ph$

(o) R = Me, R' = CH_2-(4-MeOPh)

(p) R = Me, R' = $(CH_2)_2$-(4-MeOPh)

(q) R = Me, R' = $(CH_2)_3$-(4-MeOPh)



(3) n = 1, R = Ph

(4) n = 2, R = Ph

(5) n = 2, R = CH_3

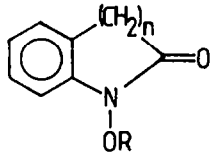
(6) n = 3, R = Ph

(7) n = 2, R = $(CH_2)_2Ph$

(8) n = 2, R = $-CH_2)_3Ph$

(9) n = 3, R = $-(CH_2)_2Ph$

(10) n = 3, R = $(CH_2)_3Ph$



(11) n = 1, R = Me

(12) n = 2, R = Me

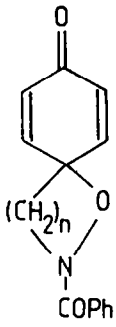
(13) n = 3, R = Me

(14) n = 2, R = $(CH_2)_2Ph$

(15) n = 3, R = $(CH_2)_2Ph$

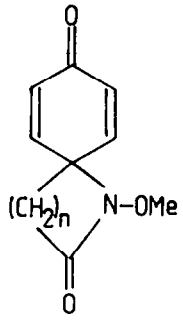
(16) n = 2, R = $(CH_2)_3Ph$

(17) n = 3, R = $(CH_2)_3Ph$



(18) n=2

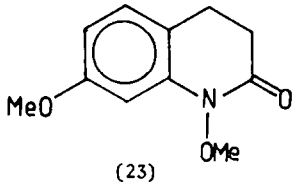
(19) n=3



(20) n=1

(21) n=2

(22) n=3



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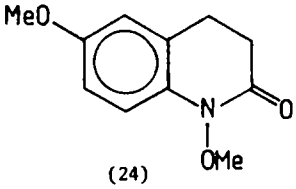

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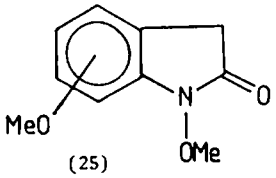

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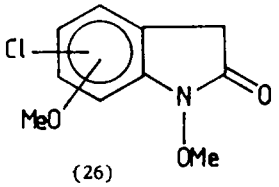

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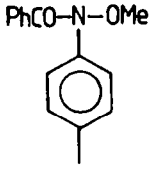

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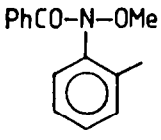

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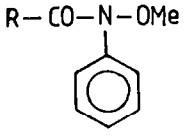
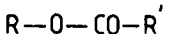


(29) R = Ph

(30) R = $(CH_2)_2Ph$

(31) R = $(CH_2)_3Ph$



(32) R = $PhCH_2$, R' = Ph

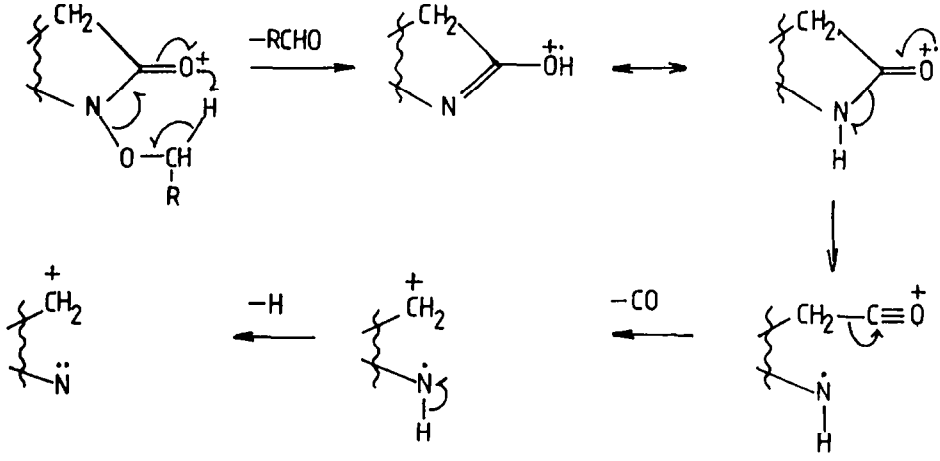
(33) R = $Ph(CH_2)_3$, R' = $(CH_2)_3Ph$

(34) R = R' = Ph

TABLE 1

Substrate	Solvent	Lewis acid	Products	
			Benzoxazine[%]	Other[%]
2b	C_6H_6	$AgBF_4$	(4)[67]	(1b)[30]
2b	C_6H_6	$AgClO_4$	(4)[81]	(1b)[20]
2b	C_6H_6	HgO	(4)[26]	-
2b	C_6H_6	$Hg(OAc)_2$	(4)[19]	-
2b	C_6H_6	$ZnBr_2$	-	(1b)[100]
2b	C_6H_6/Δ	$ZnBr_2$	-	(1b)[100]
2d	C_6H_6	$AlCl_3$	-	(1d)[100]
2d	C_6H_6	$BF_3{\cdot}Et_2O$	-	-
2b	THF	$AgBF_4$	(4)[98]	
2d	THF	$AgBF_4$	(5)[93]	
2d	Et_2O	$AgBF_4$	(5)[94]	
2d	CH_3CN	$AgBF_4$	-	(1d)[79]
2d	$CHCl_3$	$AgBF_4$	(5)[51]	(1d)[19]
2b	THF	$AgNO_3$	(4)[17]	(34)[18]
2b	THF	AgOAC	(4)[58]	(34)[19]

O-[2-(4-methoxyphenyl)ethyl]N-chlorobenzohydroxamate (2c) cyclised to the Ar_1-5 product, N-benzoyl-2-oxa-1-azaspiro-[4,5]-deca-6,9-diene-8-one (18) in 26% yield. Similarly (2f) afforded a good yield of (19). However no products arising from either Ar_2-6 or Ar_2-7 cyclisation could be detected in the respective reaction mixtures.



Scheme 1

TABLE 2

Substrate	Products [%] Cyclisation	Other	Reaction Conditions[1]
(2a)	-	(33)[67]	Et_2O/THF
(2a)	-	(33)[78]	Ag_2CO_3/CF_3CO_2H
(2b)	(4)[98]		THF
(2d)	(5)[94]		
(2c)	(6)[50]		
(2l)	(11)[25]{87}[3]		
(2m)	(12)[40]	(30)[n.d.][2]	Et_2O/C_6H_6
(2m)	(12)[55]{87}[3]		Et_2O/THF
(2n)	(13)[41]	(31)[29]	Et_2O/C_6H_6
(2n)	(13)[58]{60}[3]		Et_2O/THF
(2e)	(18)[26]		
(2f)	(19)[69]	(1f)[6]	
(2o)	(20)[10]; (25)[2]; (26)[10]		
(2p)	(21)[9]; (24)[13]	(1p)[28];	
(2q)	(22)[52]		
(2g)	(7)[65]; (14)[5]	(1g)[9]	
(2h)	(8)[80]; (15)[7]		
(2i)	(16)[26]	(1i)[17]	
(2j)	(17)[35]	(1j)[11](33)[8]	
(2k)	-	(29)[49]; (1k)[6]	Et_2O/C_6H_6
(2k)	-	(27)[24]; (28)[20]	$Et_2O/CH_3C_6H_6$

1. $AgBF_4$ in Et_2O unless otherwise specified; 2. Not determined; 3. Yields in reference 2.

When N-chloromethoxyamide (2q) was treated with $AgBF_4$ in ether, the only detectable product was consistent spectroscopically with the spiro δ-lactam (22) (table 2). Apart from δ-lactam and ketone absorptions at 1675 and 1635 cm^{-1} in the infrared spectrum and a characteristic AB system in the olefinic region of the ^1H n.m.r. spectrum, (22) displayed $[M-30]^+$ and $[M-58]^+$ mass fragments in the mass spectrum (scheme 1, R=H). The structure analysed correctly for $C_{11}H_{13}NO_3$. No Ar_2-6 product was detected. Similarly (2p) gave a low conversion to spiro γ-lactam (21) (table 2). However a second component, which was isolated in 13% yield, was identified spectroscopically as N-methoxy-6-methoxy-1H-3,4-dihydro-2-quinolone (24). The position of the methoxy group was established by 500 MHz ^1H n.m.r. spectroscopy. The aromatic resonances for (24) formed a well defined ABX system which could however accord with either (23) or (24). However decoupling experiments indicated appreciable benzylic coupling between the benzylic methylene at δ 2.65 and the X proton at δ 6.71 which is consistent with structure (24) since it is unlikely that (23) would display such a long range interaction. Treatment of (2o) with $AgBF_4$ in ether gave a mixture of three cyclised products. The first, isolated in only 10%

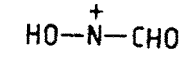
yield by preparative t.l.c., was the spiro β-lactam (20). This oil displayed a β-lactam carbonyl absorption at 1790 cm^{-1} together with a ketonic absorption at 1680 cm^{-1}. Apart from a weak M^+ at m/z 179, the mass spectrum of (20) contained typical $[M-31]^+$ (loss of methoxy) and $[M-58]^+$ fragments in accordance with other lactam fragmentations (scheme 1 R=H). A 60 MHz ^1H n.m.r. displayed singlets at δ3.8 (MeO) and δ2.95 (CH_2) as well as an AB-system in the olefinic region similar to that for (21) and (22). Two other Ar_2-5 cyclised products were isolated in low yield. Although unequivocal assignment of their structure could not be made, these were respectively (25) and an aromatic chlorinated derivative of (25), (26). Both displayed infrared γ-lactam absorptions (1730 and 1720 cm^{-1}) and two methoxy singlets in their ^1H n.m.r. spectra.

In competition reactions both O-(2-phenylethyl)-N-chloro-3-phenylpropanohydroxamate (2g) and -4-phenylbutyrohydroxamate (2h) gave 2,1-benzoxazines (7) and (8) as major products (table 2). (2g) also gave a low yield (5%) of N-(2-phenylethoxy)-1H-3,4-dihydro-2-quinolone (14) which displayed a δ-lactam carbonyl absorption at 1690 cm^{-1} and, along with a molecular ion of m/z 267, the characteristic $[M-149]^+$ fragment due to loss of phenylacetaldehyde, carbon monoxide and hydrogen (scheme 1, R=$PhCH_2$). Similarly (2h) gave the benzazepinone (15) which was characterised by its carbonyl absorption at 1675 cm^{-1} in the infrared, M^+ at m/z 281 and the mass fragment at $[M-149]^+$. N-4-phenylbutanoyl-3,4-dihydro-1H-2,1-benzoxazine (8) could not be crystallised but displayed analogous i.r. and n.m.r. features to N-benzoyl-2,1-benzoxazine (4). In addition to a molecular ion at m/z 281, the mass spectrum of (8) contained fragments at m/z 147 and 135 due to cleavage of the amide bond. N-chlorohydroxamates (2i) and (2j) cyclised only onto the acyl side-chain to give the quinolone (16) and benzazapinone (17) in low yields (table 2). Both were characterised by infrared and their characteristic fragmentations. Mass spectra of both (16) and (17) contained $[M-163]^+$ peaks due to loss of 3-phenylpropanal, CO and H according to scheme 1 (R=$Ph(CH_2)_2$-).

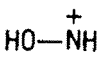
Finally, when O-methyl-N-chlorobenzohydroxamate (2k) was reacted with $AgBF_4$ in 1:1 benzene-ether mixture, a 49% yield of O-methyl-N-phenyl benzohydroxamate (29) was obtained. In addition when toluene was used in place of benzene, O-methyl-N-(4-methylphenyl) benzohydroxamate (27) and O-methyl-N-(2-methyl-phenyl)-benzohydroxamate (28) were isolated in similar yields (table 2).

DISCUSSION

The relative yields of cyclisation with silver tetrafluoroborate in various solvents indicate a strong solvent effect for the cyclisations of O-2-phenylethyl hydroxamates (2b) and (2d) (table 1). The near quantitative yields of benzoxazines in ethereal solvents suports the intermediacy of discrete nitrenium ions in these reactions (equation 1). Solvolysis of these ions in such solvents would be more effective than dipolar or dispersive interactions of chloroform or benzene. The better yields of benzolactams (11), (12) and (13) which were reported by Kikugawe and Kawase for the cyclisations in CF_3CO_2H are also explicable on this basis[2]. The interception of nitrenium ions by solvent to give modest yields of intermolecular addition products (29), (27) and (28) from (2k) when benzene and toluene were introduced as co-solvents further supports this mechanism.



(35)



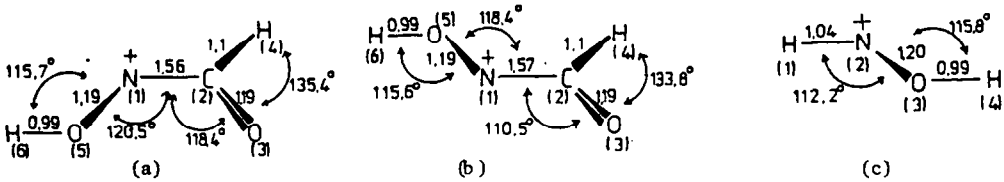
(36)

We have attributed the formation of nitrenium ions primarily to the stabilising effect of the oxygen lone pairs and support for this has been found from semi-empirical MNDO molecular orbital calculations.[1,3] A large body of evidence likewise supports the generation of N-acyl-N-aryl nitrenium ions from N-hydroxy, N-acetoxy and N-sulphonyloxy-N-arylamides.[4] Here

stabilisation and ease of formation is due to conjugation of the electron deficient nitrogen with the aryl substituent. MNDO calculations on the model N-hydroxy-N-formyl nitrenium ion (35) show substantial delocalisation of charge onto the hydroxy substituent. Table 3 gives computed charge densities, π-bond orders and LUMO coefficients for the cis- and trans- conformations of (35), as well as for N-hydroxy nitrenium ion (36). The optimised geometries for (35) and (36) are given in figure 1. The charge deficiency in (35) is in a π-molecular orbital which has major coefficients for the hydroxy oxygen and nitrogen $2p_z$ orbitals.

TABLE 3 MNDO derived properties of N-hydroxy-N-formyl nitrenium ion (35) and N-hydroxy nitrenium ion (36)

		(35)-cis	(35)-trans	(36)	
ΔH_f (kcal mol^{-1})		191,542	194,268	224,165	
π-bond orders	O····N	0,9029	0,890	0,911	
	N····C	0,1539	0,153	-	
	C····O	0,9559	0,961	-	
LUMO coefficients	O_{2p_z}	-0,533	0,525	-0,54	
	N_{2p_z}	0,789	-0,796	0,84	
	C_{2p_z}	0,165	-0,151	-	
	CO_{2p_z}	-0,257	0,254	-	
charge densities	N_1	0,1	0,12	H_1	0,22
	C_2	0,31	0,29	N_2	0,31
	O_3	-0.08	-0,04	O_3	0,1
	H_4	0,20	0,18	H_4	0,35
	O_5	0,13	0,11		
	H_6	0,32	0,33		

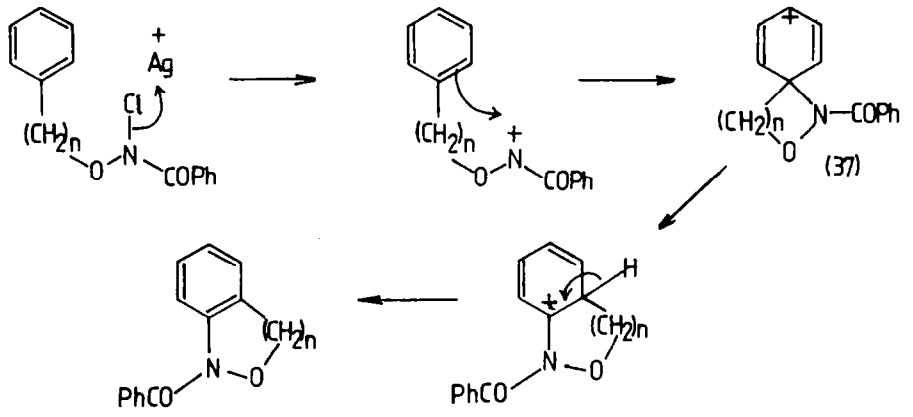


(a) (b) (c)

FIGURE1. MNDO optimised geometries for (35) cis(a), (35) trans(b) and (36) (c).

Overall charge is localised mainly on nitrogen and the hydroxy substituent. Furthermore an extremely high π-bond order (0.9) exists for the O-N bond and reflects the importance of the stabilising effect of the oxygen lone pair. Accordingly, a barrier of 29.7 $kcalmol^{-1}$ has been calculated for rotation about the N-OH bond in (35). As a comparison, hydroxy nitrenium ion (36) has a similar rotational barrier of 31.99 $kcalmol^{-1}$. MNDO computations predict only a minor energy change upon rotation about the N-CO bond in (35). These results clearly show that

the acyl substituent plays little or no role in the stability of alkoxynitrenium ions. Kikugawa's assertion that N-alkoxy-N-acyl nitrenium ions, like capto-dative free radicals[5] are stabilised by the combined donating effect of the alkoxy substituent and the withdrawing effects of the carbonyl cannot be tenable.[2]



Scheme 2

The intramolecular reactivities upon the alkoxy and acyl side-chains differ markedly in several respects. Firstly, whereas the Ar_2-5 product, indolone (11) is formed from (21) in moderate to good yields depending upon the solvent (table 2), no Ar_2-5 cyclisation onto the alkoxy side-chain of (2a) could be observed. Here the ester decomposition product (32) derived from the N,N'- diacyl-N,N'-dialkoxyhydrazine dimers were obtained in high yields.[1,6] From deuterium labelling experiments, we have shown conclusively that Ar_2-6 cyclisation of (2b) and (2d) to form benzoxazines (4) and (5) involves direct substitution of the ortho hydrogens. Ar_1-5 cyclisation to a spirane intermediate (37) (Scheme 2, n=2) is not involved although this route (Scheme 2, n=3) is preferred in the formation of benzoxazepines[7]. Thus oxazole ring formation by cyclisation onto an unactivated aryl ring on the alkoxy side-chain in (2a) or (2b) is disfavoured. In contrast, the formation of spiro-fused β-lactam (20) from (2o) albeit in low yield, is indicative that even four membered ring formation is possible when cyclisation is onto the acyl side-chain.

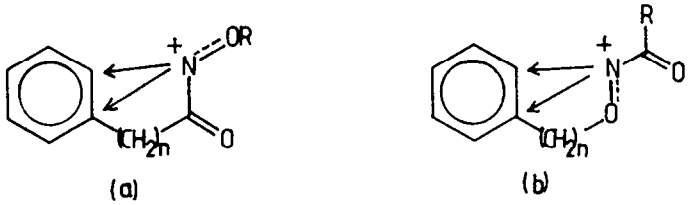
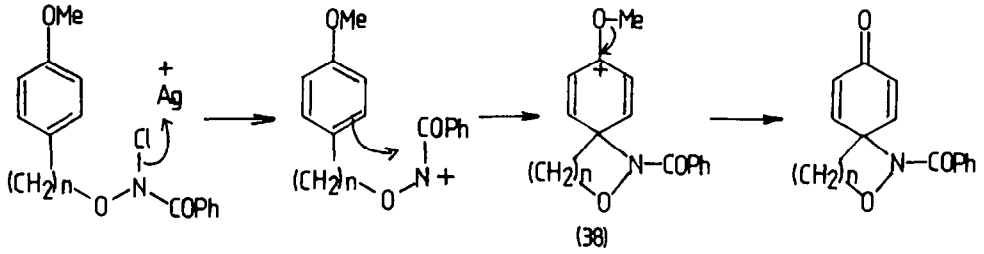


FIGURE 2. Transition states for cyclisation onto (a) the acyl and (b) the alkoxy side-chain.

These differences are more clearly understood if the transition structures for cyclisation onto the alkoxy and acyl side-chain aromatic nuclei are taken into account. The transition state structure for cyclisation onto the acyl side-chain incorporates an exocyclic pseudo π-bond between oxygen and nitrogen (figure 2a). Apparently no major barrier exists to five- or even four-membered ring formation through such a configuration. However for cyclisation onto the alkoxy side-chain, the $\overset{+}{N}$–O π-bond would be endocyclic in the transition structure (figure 2b). Although this would result in a smaller loss of rotational freedom and hence a more favourable $\Delta S^{\#}$ relative to the analogous reaction onto the acyl side-chain, it must impart more strain to the transition structure resulting in a less favourable E_A and $\Delta H^{\#}$.

The formation of (18) from (2e) indicates that the strain effects mentioned above can be overcome in five-membered ring formation if the ipso position is strongly activated to electrophilic attack by a methoxy substituent. However, the much better yield of (19) from (2f) (table 2) also reflects the expected differences in transition state strain as a result of endocyclic π-bond incorporation. In these instances, the nitrenium ion is directed to the ipso position and the resultant cationic intermediate (38, n=2,3) is stabilised by loss of methyl carbenium ion which is more favourable than a 1,2-carbon and 1,2-nitrogen migration (Scheme 3).

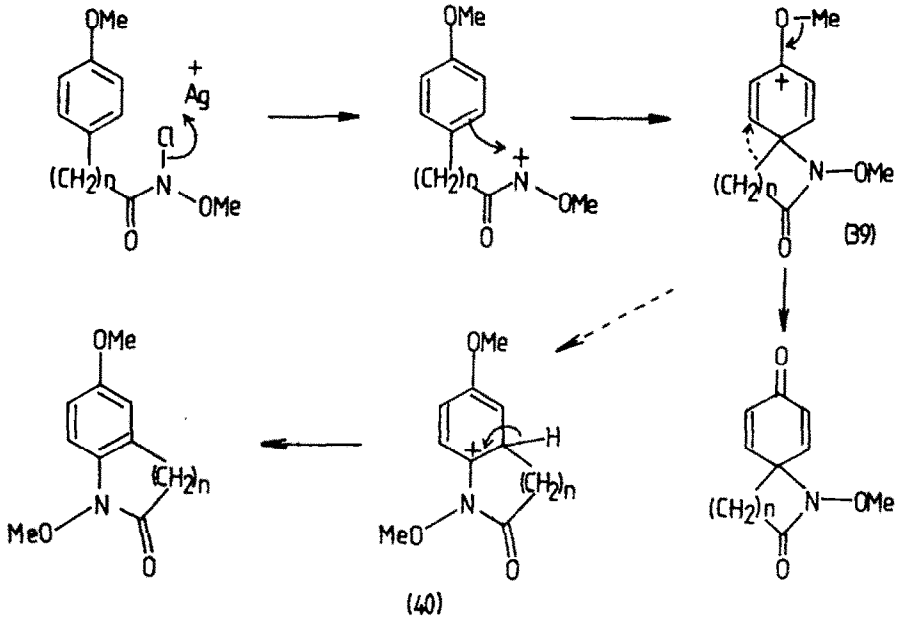


Scheme 3

A similar mechanism for benzolactam formation may likewise be operative. This mechanism (scheme 4, n=2,) would account for the formation of both γ and δ-lactam products (21) and (24) from N-chloro hydroxamate (2p). Stabilisation of intermediate (39, n=2,) by demethylation would give (21) while a 1,2-carbon migration to (40, n=2) would result in formation of (24). 1,2-carbon migration would be more favourable than a 1,2-nitrogen migration since the former process generates a carbenium ion next to nitrogen where it can be stabilised by the nitrogen lone pair. This accounts for the absence of (24) in the reaction mixture. Although the structure of the methoxy substituted N-methoxy-3H-1-indol-2-one (25) which was formed along with β-lactam (20) from (2o), could not be unequivocally assigned, such a mechanism (scheme 4, n=1,) would result in formation of the 5-methoxy derivative.

Finally such a mechanism would account for the isolation by Kikugawa and Kawase of 7-chloro- and 7-bromo-N-methoxy-3H-1-indol-2-ones from N-chloro-O-methyl-2-[2-halophenyl]ethanohydroxamates. Their mechanism involving an ipso attack at the halogen bearing carbon followed by a 1,2-halogen migration is in our opinion far less likely.[2]

The results of competition reactions are largely explicable in terms of the relative ease of ring formation reactions as well as the $\Delta S^{\#}$ for the formation of the respective transition structures (figure 2a and 2b). In the competition between benzoxazine (7) and δ-lactam (14) ring formations from (1g), the incipient N-O π-bond character in the transition structure must favour benzoxazine formation since this process involves a smaller loss of rotational freedom. The same factors, combined with the ease of generation of the smaller ring favours the formation from (1h) of benzoxazine (8) at the expense of benzazepinone (15). Likewise, the formation of only N-(3-phenyl propoxy)-3,4-dihydro-1H-quinolin-2-one (16) from (2i) is consistent with the easier formation of the smaller ring system. $\Delta S^{\#}$ for the two cyclisations would be similar in this case. Cyclisation of (2j) to the benzazepinone (17) is however spurious. The formation of similar sized rings on either side-chain should favour benzoxazepine formation [more favourable $\Delta S^{\#}$]. The formation of (17) thus suggests that the $\Delta H^{\#}$ of benzazepinone formation must be considerably less than that for benzoxazepine formation.



Scheme 4

EXPERIMENTAL

Melting points were determined on a Kofler hot stage and are uncorrected. Mass spectra were run on a Varian MAT-212 mass spectrometer equipped with a Varian SS-188 data system at the N.C.R.L./C.S.I.R. laboratories Pretoria, as well as on an AEI MS 30 double beam mass spectrometer at Rhodes University. Infra-red spectra were run on a Perkin Elmer Infra-red Spectrophotometer, Model 297. 60 MHz ^{1}H-n.m.r. spectra were recorded on a Perkin Elmer R12 A spectrometer with T.M.S. as internal standard. ^{13}C-n.m.r. spectra were recorded on a Bruker WM 500 spectrometer at the N.C.R.L./C.S.I.R. laboratories in Pretoria. Preparative separations were performed on a Waters Analytical h.p.l.c. (µporasil column) using the model 440 Absorbance detector linked to a Waters Data Module. MNDO calculations were performed on a Burroughs 6800 computer using the QCPE version of MNDO by W. Thiel[8].

2-phenylethanol, 3-phenylpropanol, 2-(p-methoxyphenyl)ethanol and 3-(p-methoxyphenylpropanol) were synthesised by $LiAlH_4$ reduction of the corresponding carboxylic acid or cinnamic acid and converted to the alkylbromides by standard procedures.[9,10] Potassium salts of hydroxamic acids were synthesised from methyl esters of the corresponding carboxylic acids and hydroxylamine by a standard procedure.[11] Potassium benzohydroxamate, cinnamohydroxamate, p-methoxyphenylaceto-hydroxamate, p-methoxycinnamohydroxamate and 4-(p-methoxyphenyl)butyrohydroxamate were isolated as solids. Potassium acetohydroxamate, phenylacetohydroxamate and 4-phenylbutyhydroxamate were viscous semi-solids which were used as such.

General procedure for the synthesis of O-alkyl hydroxamates

A solution of the appropriate potassium hydroxamate, an equimolar amount of alkyl halide, and a 10% molar excess of sodium carbonate were stirred overnight at room temperature in a 1:1 mixture of methanol and water and then refluxed for two hours. After removal of the methanol under reduced pressure, the residue was acidified with dilute HCl and extracted with dichloromethane. Combined extracts were washed with water and aqueous sodium thiosulphate (where methyl iodide was the alkyl halide) and dried (Na_2SO_4). Concentration under reduced pressure afforded O-alkyl hydroxamate which was purified by crystallisation or preparative h.p.l.c. on silica gel (chloroform as mobile phase). The synthesis of O-(2-phenylethyl) benzohydroxamate (1b), O-(2-phenylethyl)acetohydroxamate(1d) and O-(3-phenylpropyl)benzohydroxamate (1c) have been described previously.[1]

O-Benzyl benzohydroxamate (1a)

Benzyl chloride (7,22g; 0,057 mol) and potassium benzohydroxamate afforded after recrystallisation from benzene pure O-benzyl benzohydroxamate (10g) as colourless needles, m.p. 103-104°C. ν_{max} ($CHCl_3$) 3400, 3250, 3000, 1690 and 1610 cm^{-1}; δ($CDCl_3$) 5,02 (2H, s), 7,35 - 7,58 (8H, m), 7,65 - 7,88 (2H, m). M^+ 227, m/z 121, 105, 91 and 77. (Found: C 74,2; H 5,65; N 6,25%. $C_{14}H_{13}NO_2$ requires C 73,99; H 5,77; N 6,16%.

O-[2-(p-Methoxyphenyl)ethyl] benzohydroxamate (1e)
2-[p-Methoxyphenyl]bromoethane (8,63g; 0,040 mol) and potassium benzohydroxamate gave after chromatography and decolourisation with charcoal an oil which crystallised on standing. Recrystallisation from benzene-petroleum ether yielded pure O-[2-(p-methoxyphenyl)ethyl] benzohydroxamate (3,60g) m.p. 83 - 84,5°C. ν_{max} ($CHCl_3$) 3410, 3275, 3000, 2950, 1690 and 1619 cm^{-1}; δ($CDCl_3$) 2,89 (2H, t), 3,70 (3H, s), 4,12 (2H, t), 6,62 and 7,09 (4H, 2xd, J 8,66 Hz), 7,20 - 7.52 (3H, m), 7,60 - 7,82 (2H, m). M^+ 271 (trace), $^m/_z$ 134, 121 and 105. (Found: C 70,9; H 6,1; N 5,2%. $C_{16}H_{17}NO_3$ requires C 70,83; H 6,32; N 5,16%).

O-[3-(p-Methoxyphenyl)-1-propyl] benzohydroxamate (1f)
Potassium benzohydroxamate (10,82g; 0,062 mol) and 3-(p-methoxyphenyl)-1-bromopropane afforded after recrystallisation from ether-petroleum ether O-[3-(p-methoxyphenyl)-1-propyl] benzohydroxamate (4,90g) m.p. 79-81°C. ν_{max} ($CHCl_3$) 3410, 3020, 1690 and 1610 cm^{-1}; δ($CDCl_3$) 1,88 (2H, m), 2,60 (2H, t), 3,69 (3H, s), 3,93 (2H, t), 6,71 and 7,01 (4H, 2xd, J 7,98 Hz). 7,20 - 7,48 (3H, m), 7,65 - 7,90 (2H, m). M^+ 285, $^m/z$ 240, 148, 134 and 121. (Found: C 71,34; H 6,65; N 4,95%). $C_{17}H_{19}NO_3$ requires C 71,56; H 6,71; N 4,91%).

O-[2-Phenylethyl] 3-phenylpropanohydroxamate (1g)
Potassium cinnamohydroxamate (11,47g; 0,057 mol) and 2-phenylbromoethane afforded after chromatography an oil which crystallised on standing. Recrystallisation from benzene-petroleum ether gave O-(2-phenylethyl) cinnamohydroxamate (4,81g), m.p. 83 - 83,5°C. ν_{max} ($CHCl_3$) 3390, 3010, 1670, and 1630 cm^{-1}; δ($CDCl_3$) 2,97 (2H, t), 4,16 (2H, t), 6,50 and 7,71 (2H, 2xd, J 16 Hz), 7,20 (5H, s), 7,31 (5H, s). M^+ 267, $^m/z$ 163, 131 and 103. (Found: C 76,45; H 6,3; N 5,25%. $C_{17}H_{17}NO_2$ requires C 76,38; H 6,41; N 5,24%. Hydrogenation of O-(2-phenylethyl) cinnamohydroxamate (4,00g; 0,015 mol) in ethyl acetate (150 ml) over Adam's catalyst followed by preparative t.l.c. (silica gel/$CHCl_3$) of the crude product yielded pure O-(2-phenylethyl) 3-phenylpropanohydroxamate as an oil which crystallised on standing, m.p. 60 - 62°C. ν_{max} ($CHCl_3$) 3410, 3250, 2950, 1680 and 1610 cm^{-1}; δ($CDCl_3$) 2,34 (2H,t), 2,81 (2H, t), 2,88 (2H, t), 3,94 (2H, t), 7,13 (10H, s). M^+ 269, $^m/z$ 165, 133 and 105. (Found: C 75,5; H 6,85; N 5,15%. $C_{17}H_{19}NO_2$ requires C 75,81; H 7,11; N 5,20%).

O-[2-Phenylethyl] 4-phenylbutyrohydroxamate (1h)
Potassium 4-phenylbutyrohydroxamate (11,74g; 0,0504 mol) and 2-phenylbromoethane afforded a solid (10,72g). Recrystallisation from benzene-petroleum ether gave O-(2-phenylethyl) 4-phenylbutyrohydroxamate (5,79g), m.p. 88,5 - 90°C. ν_{max} ($CHCl_3$) 3410, 2900, 1690 and 1610 cm^{-1}; δ($CDCl_3$) 1,80 - 2,15 (4H, m), 2,55 (2H, t), 2,87 (2H, t), 4,00 (2H, t), 7,18 (10H, s). M^+ 283, $^m/z$ 179, 147 and 105. (Found: C 76,35; H 7,5; N 5,0%. $C_{18}H_{21}NO_2$ requires C 76,30; H 7,47; N 4,94%).

O-[3-Phenyl-1-propyl] 3-phenylpropanohydroxamate (1i)
Potassium cinnamohydroxamate (7,21g; 0,036 mol) and 3-phenyl-1-bromopropane gave after chromatography O-(3-phenyl-1-propyl)cinnamohydroxamate as an oil which crystallised to a low-melting solid (5,35g) on standing. ν_{max} ($CHCl_3$) 3400, 3250, 3010, 2900, 1680 and 1640 cm^{-1}; δ($CDCl_3$) 1,91 (2H, m), 2,66 (2H, t), 3,96 (2H, t), 6,69 and 7,73 (2H, 2xd, J 15,3 Hz), 6,99 - 7,45 (10H, m). (Found: C 77,34; H 6,66; N 5,05%. $C_{18}H_{19}NO_2$ requires C 76,84; H 6,81; N 4,98%). Hydrogenation of O-(3-phenyl-1-propyl) cinnamohydroxamate (3,60g; 0,013 mol) in ethyl acetate (100 ml) over Adam's catalyst followed by preparative t.l.c. (silica gel/$CHCl_3$) yielded pure O-(3-phenyl-1-propyl) 3-phenylpropanohydroxamate as a low-melting solid (3,67g). ν_{max} ($CHCl_3$) 3410, 3275, 2900, 1690 and 1610 cm^{-1}; δ($CDCl_3$) 1,81 (2H, m), 2,49 (2H, t), 2,76 (2H, t), 3,73 (2H, t), 7,13 (10H, s). M^+ 283, $^m/z$ 150, 149, 133, 118, 117, 106, 105 and 104. (Found: C 76,5; H 7,25; N 4,7%. $C_{18}H_{21}NO_2$ requires C 76,30; H 7,47; N 4,94%).

O-(3-Phenyl-1-propyl) 4-phenylbutyrohydroxamate (1j)
Potassium 4-phenylbutyrohydroxamate (16,37g; 0,075 mol) and 3-phenyl-1-bromopropane gave after chromatography and decolourisation with charcoal O-(3-phenyl-1-propyl) 4-phenylbutyrohydroxamate (10,0g) as an oil. ν_{max} ($CHCl_3$) 3420, 3010, 2950, 1690 and 1610 cm^{-1}; δ($CDCl_3$) 1,70 - 2,05 (6H, m), 2,41 - 2,82 (4H, m), 3,80 (2H, m), 7,15 (10H, m) M^+ 297, $^m/z$ 192, 147, 118, 117, 105 and 104. (Found: C 76,6; H 7,7; N 4,2%. $C_{19}H_{23}NO_2$ requires C 76,74; H 7,80; N 4,71%).

O-Methyl benzohydroxamate (1k)
Potassium benzohydroxamate (30,00g; 0,171 mol) and methyl iodide gave after chromatography, O-methyl benzohydroxamate as a low melting solid (13,72g). ν_{max} ($CHCl_3$) 3410, 3250, 3000, 2950, 1680 and 1610 cm^{-1}; δ($CDCl_3$) 3,72 (3H, s), 7,35 - 7,49 (3H, m), 7,70 - 7,89 (2H, m). M^+ 151, $^m/z$ 121 and 105. Correct elemental analysis could not be obtained for this material.

O-Methyl phenylacetohydroxamate (1l)
Potassium phenylacetohydroxamate (8,00g; 0,042 mol) and methyl iodide gave after recrystallisation from benzene-petroleum ether O-methyl phenylacetohydroxamate (3,0g) m.p. 69 - 71°C. ν_{max}($CHCl_3$) 3410, 3000 and 1695 cm^{-1}; δ($CDCl_3$) 3,39 (2H, s), 3,62 (3H, s); 7,23 (5H, s). M^+ 165, $^m/z$ 134, 118 and 91. (Found: C 65,55; H 6,5; N 8,5%. $C_9H_{11}NO_2$ requires C 65,44; H 6,71; N 8,48%).

O-Methyl 3-phenylpropanohydroxamate (1m)
Potassium cinnamohydroxamate (20,00g; 0,099 mol) and methyl iodide gave after recrystallisation from benzene-petroleum ether colourless needles of O-methyl cinnamohydroxamate (13,0g) m.p. 91 - 92°C. ν_{max} ($CHCl_3$) 3400, 3225, 3010, 1670 and 1635 cm^{-1}; $\delta(CDCl_3)$ 3,81 (3H, s), 6,62 and 7,73 (2H, 2xd, J 15,3 Hz) 7,20 - 7,55 (5H, m). M^+ 177/176, m/z 146, 131, 128 and 103. (Found: C 68,05; H 6,4; N 7,9%. $C_{10}H_{11}NO_2$ requires C 67,78; H 6,26; N 7,90%). Hydrogenation of O-methyl cinnamohydroxamate (3,00g; 0,028 mol) over Adam's catalyst in ethyl acetate afforded O-methyl 3-phenylpropanohydroxamate as a colourless oil (5,0g). ν_{max} ($CHCl_3$) 3410, 3250, 3000, 2950, 1680 and 1610 cm^{-1}; $\delta(CDCl_3)$ 2,40 (2H, t), 2,94 (2H,t), 3,59 (3H, s), 7,19 (5H, s). M^+ 179, m/z, 149, 133, 131 and 105. (Found: C 67,3; H 7,5; N 7,8%. $C_{10}H_{13}NO_2$ requires C 67,02; H 7,31; N 7,82%).

O-Methyl 4-phenylbutyrohydroxamate (1n)
Potasssium 4-phenylbutyrohydroxamate (52,00g; 0,239 mol) and methyl iodide gave after chromatography and recrystallisation from ether-petroleum ether fine colourless needles of O-methyl 4-phenylbutyrohydroxamate (11,0g), m.p. 58,5 - 60,5°C. ν_{max} ($CHCl_3$) 3415, 3250, 3010, 2950, 1690 and 1610 cm^{-1}; $\delta(CDCl_3)$ 2,08 (4H, m), 2,60 (2H, t), 3,65 (3H, s), 7,19 (5H, s). M^+ 193, m/z 147, 129 and 91. (Found: C 68,6; H 7,95; N 7,25%. $C_{11}H_{15}NO_2$ requires C 68,37; H 7,82; N 7,25%).

O-Methyl (p-methoxyphenyl)acetohydroxamate (1o)
Potassium (p-methoxyphenyl)acetohydroxamate (10,00g; 0,046 mol) and methyl iodide gave after recrystallisation from benzene colourless needles of O-methyl (p-methoxyphenyl)acetohydroxamate (3,6g), m.p. 83 - 85°C. ν_{max} ($CHCl_3$) 3400, 2950, 1690 and 1619 cm^{-1}; $\delta(CDCl_3)$ 3,41 (2H, s), 3,65 (3H, s), 3,76 (3H, s), 6,80 and 7,17 (4H, 2xd, J 9,33 Hz). M^+ 195, m/z 148 and 121. (Found: C 62,25; H 6,35; N 6,85%. $C_{10}H_{13}NO_3$ requires C 61,53; H 6,71; N 7,17%).

O-Methyl 3-(p-methoxyphenyl)propanohydroxamate (1p)
Potassium p-methoxycinnamodhydroxamate (30,00g; 0,130 mol) and methyl iodide gave after recrystallisation from benzene-petroleum ether O-methyl p-methoxycinnamohydroxamate (10,0g), m.p. 132 - 135°C. ν_{max} ($CHCl_3$) 3400, 3000, 1675, 1635, and 1610 cm^{-1}; $\delta(CDCl_3)$ 3,79 (6H, s), 6.41 and 7,68 (2H, 2xd, J 16,3 Hz), 6,81 and 7,42 (4H, 2xd, J 9,3 Hz). M^+ 207, m/z 176, 161 and 133. (Found: C 63,9; H 6,15; N 6,9%. $C_{11}H_{13}NO_3$ requires C 63,76; H 6,32; N 6,76%). Hydrogenation of O-methyl p-methoxycinnamohydroxamate (2,28g; 0,011 mol) over Adam's catalyst in methanol and recrystallisation from diethyl ether yielded O-methyl 3-(p-methoxyphenyl)-propanohydroxamate (1,5g), m.p. 70 - 71° (with sublimation). ν_{max} ($CHCl_3$) 3400, 3000, 1680 and 1620 cm^{-1}; $\delta(CDCl_3)$ 2,48 (2H, broad t), 2,89 (2H, t), 3,51 (3H, s), 3,72 (3H, s), 6,77 and 7,10 (4H, 2xd, J 8,66 Hz). M^+ 209, m/z 178, 135 and 121. (Found: C 63,3; H 7,0; N 6,8%. $C_{11}H_{15}NO_3$ requires C 63,14; H 7,23; N 6,69%).

O-Methyl 4-(p-methoxyphenyl)butyrohydroxamate (1q)
Potassium 4-(p-methoxyphenyl)butyrohydroxamate (6,00g; 0,024 mol) and methyl iodide gave after recrystallisation from ether-petroleum ether O-methyl 4-(p-methoxyphenyl)butyrohydroxamate (3,0g), m.p. 45°C (with sublimation). ν_{max} ($CHCl_3$) 3410, 3250, 2950, 1680 and 1619 cm^{-1}; $\delta(CDCl_3)$ 2,07 (4H, m), 2,55 (2H, t), 3,66 (3H, s), 3,70 (3H, s), 6,78 and 7,08 (4H, 2xd, J 8,91 Hz). M^+ 223, m/z 178, 134 and 121. (Found: C 64,75; H 7,75; N 6,3%. $C_{12}H_{17}NO_3$ requires C 64,55; H 7,67; N 6,27%).

General procedure for N-chlorination of alkylbenzohydroxamates

Procedure A

A solution of the appropriate amide or hydroxamate in either anhydrous benzene or dichloromethane was stirred for two hours in the dark with a three molar excess of t-butylhypochlorite[12]. Removal of the solvent at 30°C under reduced pressure afforded the N-chlorohydroxamate as a yellow oil whose purity was determined by iodometry.

Procedure B

The above procedure was modified[13] in the case of those amides or hydroxamates which were resistant to N-chlorination. One drop of bromine was added to the reaction mixture after addition of the t-butylhypochlorite followed by stirring in the light for two hours. Spectral and analytical data are reported with the individual compounds.

Synthesis of N-chlorobenzohydroxamates (2b), (2c) and (2d) have been described previously[1].

O-Benzyl N-chlorobenzohydroxamate (2a)
O-Benzyl benzohydroxamate (1a) (2,00g; 8,8 mmol) was treated according to Procedure A to yield O-benzyl N-chlorobenzohydroxamate (2,3g). ν_{max} ($CHCl_3$) 1730 cm^{-1}; $\delta(CDCl_3)$ 5,01 (2H, s), 7,15 - 7,53 (8H, m), 7,55 - 7,76 (2H, m). [Found: Cl (by iodometry), 12,87%. $C_{14}H_{12}ClNO_2$ requires Cl, 13,55%].

O-[2-(p-Methoxyphenyl)ethyl] N-chlorobenzohydroxamate (2e)
O-[2(p-Methoxyphenyl)ethyl] benzohydroxamate (1e) (1,84g; 6,8 mmol) was treated according to Procedure B to yield a yellow oil (2,1g). N.m.r. spectroscopy indicated a mixture of the N-chloro adduct and the parent hydroxamate. Iodometry revealed the mixture to contain 52% of the N-chloro adduct. Attempts to improve the yield of the N-chlorohydroxamate were unsuccessful and the mixture decomposed when chromatographed. Consequently the mixture was used as such. ν_{max} ($CHCl_3$) 1725 cm^{-1}; $\delta(CDCl_3)$ 2,78 (2H, t), 3,65 (3H, s), 4,21 (2H, t), 6,67 and 6,97 (4H, 2xd, J 8,46 Hz), 7,21 - 7,40 (3H, m), 7,55 - 7,72 (2H, m). [Found: Cl (by iodometry), 6,03%. $C_{16}H_{16}ClNO_3$ requires Cl, 11,59%].

O-[3-(p-Methoxyphenyl)-1-propyl] N-chlorobenzohydroxamate (2f)
O-[3-p-Methoxyphenyl)-1-propyl] benzohydroxamate (1f) (1,00g; 3,5 mmol) was treated according to Procedure B to yield O-[3-(p-methoxyphenyl)-1-propyl] N-chlorobenzohydroxamate (1,12g). ν_{max} ($CHCl_3$) 1725 cm^{-1}; $\delta(CDCl_3)$ 1,83 (2H, m), 2,50 (2H, t), 3,67 (3H, s), 4,01 (2H, t), 6,67 and 6,94 (4H, 2xd, J 8,53 Hz), 7,21 - 7,54 (3H, m), 7,61 - 7,83 (2H, m). [Found: Cl (by iodometry), 10,8%. $C_{17}H_{18}ClNO_3$ requires Cl, 11,09%].

O-(2-Phenylethyl) N-chloro-3-phenylpropanohydroxamate (2g)
O-(2-Phenylethyl) 3-phenylpropanohyroxamate (1g) (2,00g,7,4 mmol) was treated according to Procedure A, to yield O-(2-phenylethyl) N-chloro-3-phenylpropanohydroxamate (2,13g). ν_{max} ($CHCl_3$) 1735 cm^{-1}; $\delta(CDCl_3$ 2,45 - 2,79 (4H, m), 2,88 (2H, t), 4,14 (2H, t) and 6,95 - 7,25 (10H, broad s). [Found: Cl (by iodometry), 11,7%. $C_{17}H_{18}ClNO_2$ requires Cl, 11,67%].

O-(2-Phenylethyl) N-chloro-4-phenylbutyrohydroxamate (2h)
O-(2-Phenylethyl) 4-phenylbutyrohydroxamate (1h) (3,00g; 10,5 mmol) was treated according to Procedure A to yield O-(2-phenylethyl) N-chloro-4-phenylbutyrohydroxamate (3,5g). ν_{max} ($CHCl_3$) 1740 cm^{-1}; $\delta(CDCl_3)$ 1,58 - 2,05 (2H, m), 2,10 - 2,60 (4H, m), 2,83 (2H, t), 4,12 (2H, t), 6,95 - 7,30 (10H, broad s). [Found: Cl (by iodometry), 10,5%. $C_{18}H_{20}ClNO_2$ requires Cl, 11,16%].

O-(3-Phenyl-1-propyl) N-chloro-3-phenylpropanohydroxamate (2i)
O-(3-Phenyl-1-propyl) 3-phenylpropanohydroxamate (1i) (3,00g; 10,6 mmol) was treated according to Procedure A affoording O-(3-phenyl-1-propyl) N-chloro-3-phenylpropanohydroxamate (3,4g). ν_{max} ($CHCl_3$ 1750 cm^{-1}; $\delta(CDCl_3)$ 1,79 - 2,15 (2H, m), 2,50 - 2,95 (6H, m), 3,89 (2H, t) and 7,05 - 7,35 (10H, broad s). [Found: Cl (by iodometry), 10,2%. $C_{18}H_{20}ClNO$ requires Cl, 11,15%].

O-(3-Phenyl-1-propyl) N-chloro-4-phenylbutyrohydroxamate (2j)
O-(3-Phenyl-1-propyl) 4-phenylbutyrohydroxamate (1j) (4,00g; 0,0134 mol) treated according to Procedure A yielded a mixture of the N-chloro derivative and the parent hydroxamate (i.r.). The crude mixture was chromatographed through a short silica gel column with carbon tetrachloride as eluent. Concentration of the eluent at 30°C under vacuum afforded O-(3-phenyl-1-propyl) N-chloro-4-phenylbutyrohydroxamate (1,45g). ν_{max} ($CHCl_3$) 1735 cm^{-1}; $\delta(CDCl_3)$ 1,91 (2H, m), 2,45 - 2,81 (4H, m), 2,87 (4H, broad s), 3,91 (2H, t), 7,18 (10H, broad s). [Found: Cl (by iodometry), 9,5%. $C_{19}H_{22}NO_2Cl$ requires Cl, 10,68%].

O-Methyl N-chlorobenzohydroxamate (2k)
O-Methyl benzohydroxamate (1k) (9,00g; 0,054 mol) was treated according to Procedure A to yield a mixture of the N-chloro derivative and the parent hydroxamate (i.r.). The mixture was chromatographed through a short silica gel column with carbon tetrachloride as eluent. Concentraion of the eluent at 30°C under reduced pressure yielded O-methyl N-chlorobenzohydroxamate (7,0g). ν_{max} ($CHCl_3$) 1730 cm^{-1}; $\delta(CDCl_3)$ 3,73 (3H, s), 7,23 - 7,52 (3H, m), 7,60 - 7,82 (2H, m). [Found: Cl (by iodometrey), 16,0%. $C_9H_{10}ClNO_2$ requires Cl, 17,76%].

O-Methyl N-chlorophenylacetohydroxamate (2l)
O-Methyl phenylacetohydroxamate (1l) (1,83g; 11,1 mmol) was treated according to Procedure A to yield O-methyl N-chlorophenylacetohydroxamate (2,19g). ν_{max} $(CHCl)_3$ 1735 cm^{-1}; $\delta(CDCl_3)$ 3,61 (3H, s), 3,81 (2H, s), 7,22 (5H, s). [Found: Cl (by iodometry), 17,8%. $C_9H_{10}ClNO_2$ requires 17,76%].

O-Methyl- N-chloro-3-phenylpropanohydroxamate (2m)
O-Methyl 3-phenylpropanohydroxamate (1m), (1,00g; 5,6 mmol) was treated according to Procedure A to yield O-methyl N-chloro-3-phenylpropanohydroxamate (1,2g). ν_{max} ($CHCl_3$) 1740 cm^{-1}; $\delta(CDCl_3)$ 2,75 - 2,98 (4H, m) 3,73 (3H, s) and 7,15 (5H, s). [Found: Cl (by iodometry), 16,6%. $C_{10}H_{12}ClNO_2$ requires Cl, 16,59%].

O-Methyl N-chloro-4-phenylbutyrohydroxamate (2n)
O-Methyl 4-phenylbutyrohydroxamate (1n) (2,00g; 10,3 mmol) was treated according to Procedure A to yield O-methyl N-chloro-4-phenylbutyrohydroxamate (2,35g). ν_{max} ($CHCl_3$) 1740 cm^{-1}; $\delta(CDCl_3)$ 1,94 (2H, m), 2,48 (2H, t), 2,69 (2H, t), 3,68 (3H, s), 7,10 (5H, s). [Found: Cl (by iodometry), 15,6%. $C_{11}H_{14}ClNO_2$ requires Cl, 15,57%].

O-Methyl N-chloro-(p-methoxyphenyl)acetohydroxamate (2o)
O-Methyl (p-methoxyphenyl)acetohydroxamate (1o) (1,00g; 5,1 mmol) was treated according to Procedure A, to yield O-methyl N-chloro-(p-methoxyphenyl)acetohydroxamate (1,2g). ν_{max} ($CHCl_3$) 1735 cm^{-1}; $\delta(CDCl_3)$ 3,68 (3H, s), 3,71 (3H, s), 3,79 (2H, s), 6,85 and 7,16 (4H, 2xd, J 8,66 Hz). [Found: Cl (by iodometry), 14,1%. $C_{10}H_{12}ClNO_3$ requires Cl, 15,43%].

O-Methyl N-chloro-3-(p-methoxyphenyl)propanohydroxamate (2p)
O-Methyl 3-(p-methoxyphenyl)propanohydroxamate (1p) (1,00g; 4,8 mmol) was treated using Procedure A to yield the O-methyl N-chloro-3-(p-methoxyphenyl)-propanohydroxamate (1,2g). ν_{max} ($CHCl_3$) 1740 cm^{-1}; δ($CDCl_3$) 2,87 (4H, broad s), 3,73 (6H, s), 6,33 and 7,16 (4H, 2xd, J 8,20 Hz). [Found: Cl (by iodometry), 13,0%. $C_{11}H_{14}ClNO_3$ requires Cl, 14,55%].

O-Methyl N-chloro-4-(p-methoxyphenyl)butyrohydroxamate (2q)
O-Methyl 4-(p-methoxyphenyl)butyrohydroxamate (1q) (2,00g; 9,0 mmol) was treated according to Procedure B to yield O-methyl N-chloro-4-(p-methoxyphenyl)butyrohydroxamate (2,3g). ν_{max} ($CHCl_3$) 1740 cm^{-1}; δ($CDCl_3$) 1,99 (2H, m), 2,35 - 2,75 (4H, m), 3,68 (3H, s), 3,71 (3H, s), 6,78 and 7,07 (4H, 2xd, J 8,33 Hz). [Found: Cl (by iodometry), 12,9%. $C_{12}H_{16}ClNO_3$ requires Cl, 13,76%.

General procedures for the reaction of O-alkyl-N-chlorohydroxamates with Lewis acids

N-acetyl-and N-benzoyl-3,4-dihydro-1H-2,1-benzoxazines (4) and (5)
The formation of N-benzoyl-3,4-dihydro-1H-2,1-benzoxazine (4) from O-(2-phenylethyl)-N-chloro-benzohydroxamate (2b) in benzene with $AgBF_4$, $AgClO_4$, HgO and $Hg(OAC)_2$ as well as the formation of N-acetyl-3,4-dihydro-1H-2,1- benzoxazine (5) from O-(2-phenylethyl)-N-chloro-acetohydroxamate (2d) in benzene with $AgBF_4$ have been described elsewhere.[1] The yields and products from the reactions of (2b) and/or (2d) in THF, diethyl ether, acetonitrile and chloroform with various silver salts are given in Table 1. The formation of N-acetyl-3,4-dihydro-1H-2,1-benzoxazine (5) from (2d) in diethylether with $AgBF_4$ is exemplary:

O-(2-phenylethyl) N-chloroacetohydroxamate (2d) (1,07g; 5 mmol) in diethylether (30 ml) was stirred for six hours in the dark with silver tetrafluoroborate (0,97g; 5,0 mmol) when an aliquot, tested with aqueous potassium iodide/acetic acid was negative in positive halogen. The reaction mixture was filtered and the precipitate was washed with chloroform. The combined chloroform washings and ether filtrate were washed with water, dried (Na_2SO_4), and concentrated under reduced pressure to a brown oil (0,83g) which crystallised as N-acetyl-3,4-dihydro-1H-2,1-benzoxazine (5) (94%) and was identical (n.m.r.,m.p.) to authentic material.[1]

N-benzoyl-1,3,4,5-tetrahydro-2,1-benzoxazepine (6)
O-(3-phenyl-1-propyl) N-chlorobenzohydroxamate (2c) (1,36g; 4,7 mmol) in diethyl ether (100 ml) was stirred overnight with silver tetrafluoroborate (0,91g; 4,7 mmol). Work-up by the general procedure gave a mixture from which N-benzoyl-1,3,4,5-tetrahydro-2,1-benzoxazepine (6) was isolated, in 50% yield by preparative t.l.c. and was identical to authentic material.[1]

Reaction of O-benzyl N-chlorobenzohydroxamate (2a)
(i) with silver tetrafluoroborate in diethyl ether-tetrahydrofuran.
O-Benzyl N-chlorobenzohydroxamate (2a) (1,15g; 4,4 mmol) in a 1:1 diethyl ether-tetrahydrofuran mixture (50 ml) was stirred in the dark for one hour with silver tetrafluoroborate (0,86g; 4,4 mmol). Work-up yielded a brown oil (4,28 g) which after column chromatography (silica gel/$CHCl_3$) afforded benzyl benzoate (32) (0,63g; 67,5%) which was identical to authentic material (n.m.r., i.r., t.l.c.).
(ii) with silver carbonate in diethyl ether-trifluoroacetic acid.
O-Benzyl N-chlorobenzohydroxamate (2a) (2,2g; 8,4 mmol) in diethyl ether (50 ml) was added to a cooled, stirred suspension of silver carbonate (1,24g; 4,5 mmol) in a mixture of diethyl ether (50 ml) and trifluoroacetic acid (10 ml). Stirring was continued overnight at room temperature. The reaction mixture was filtered and the filtrate washed successively with aqueous sodium carbonate and water, dried (Na_2SO_4) and concentrated to a pale yellow oil (1,63g). Analysis by n.m.r. spectroscopy revealed mainly benzyl benzoate (32) (78%).
No cyclic products nor parent hydroxamate (1a) were detected in these reaction mixtures.

Reaction of O-[2-(p-methoxyphenyl)ethyl] N-chlorobenzohydroxamate (2e)
O-[2-(p-Methoxyphenyl)ethyl] N-chlorobenzohydroxamate (2e) (1,03g; 3,4 mmol) contaminated with its parent hydroxamate (1e) (0,8g; 2,95 mmol) in diethyl ether (50 ml) was stirred overnight with silver tetrafluoroborate (0,68g; 3,5 mmol). Work-up and preparative t.l.c. yielded N-benzoyl-2-oxa-1-azaspiro[4,5]deca-6,9-diene-8-one (18) as a solid (0,22g; 26,12%). The pure compound was obtained after recrystallisation from benzene-petroleum ether m.p. 154 - 156°C. M^+ 255, $^m/_z$ 225, 105 and 77; ν_{max} ($CHCl_3$) 1675 and 1640 cm^{-1}; δ($CDCl_3$) 2,54 (2H, t), 4,21 (2H, t), 6,24 and 7,88 (4H, 2xd, J 10,5 Hz), 7,26 - 7,51 (3H, m) and 7,67 - 7,85 (2H, m). (Found: C 70,6; H 5,15; N 5,5%. $C_{15}H_{13}NO_3$ requires C 70,57; H 5,13; N 5,49%). Also isolated was the parent O-[2-(p-methoxyphenyl)ethyl] benzohydroxamate (1e) (0,80g), identical to authentic material (n.m.r., i.r.).

Reaction of O-[3-(p-methoxyphenyl)-1-propyl] N-chlorobenzohydroxamate (2f)
A solution of O-[3-(p-methoxyphenyl)-1-propyl] N-chlorobenzohydroxamate (2f) (1,60g 5,0 mmol) in diethyl ether (50 ml) was stirred overnight with silver tetrafluoroborate (0,97 g; 5,0 mmol) under the general conditions. Work-up yielded a brown gum (1,48g) which upon preparative t.l.c. gave two major components. The more polar of these was identified by n.m.r. spectroscopy and t.l.c. as the parent hydroxamate (1f) (0,08g; 5,61%). The second component (0,93g) recrystallised from benzene-petroleum ether as N-benzoyl-2-oxa-1-azaspiro[5,5]undeca-7,10-diene-9-one (19) (69,1%) m.p. 134,5 - 135,5°C. M^+ 269, $^m/_z$ 239, 164, 105 and 77, ν_{max}($CHCl_3$) 1670 and 1630 cm^{-1}; δ($CDCl_3$) 1,88 (4H, m), 4,13 (2H, m), 6,21 and 7,21 (4H, 2xd, J 10,66 Hz) and 7,2 - 7,75 (5H, m). (Found: C 71,4; H 5,55; N 5,25%. $C_{16}H_{15}NO_3$ requires C 71,36; H 5,61; N 5,20%).

Reaction of O-(2-phenylethyl) N-chloro-3-phenylpropanohydroxamate (2g)
An ether solution (50 ml) of O-(2-phenylethyl) N-chloro-3-phenylpropano-hydroxamate (2g) (2,13g; 7,0 mmol) containing silver tetrafluoroborate (1,36g; 7,0 mmol) was stirred overnight in the dark. Work-up and preparative t.l.c. gave N-(3-phenylpropanoyl)-3,4-dihydro-1H-2,1-benzoxazine (7) (1,22g; 65,20%) m.p. 67 - 69°C from benzene-petroleum ether. M^+ 267, $^m/_z$ 135, 105 and 91; ν_{max} ($CHCl_3$) 1675 and 1390 cm^{-1}; $\delta(CDCl_3)$ 2,70 (2H, t), 2,75 - 3,01 (4H, m), 3,92 (2H, t), 6,89 - 7,05 (3H, m), 7,15 (5H, s) and 7,85 - 8,19 (1H, m). (Found: C 76,35; H 6,35; N 5,25%. $C_{17}H_{17}NO_2$ requires C 76,38; H 6,41; N 5,24%).
Secondly, N-(2-phenylethoxy)-3,4-dihydro-1H-quinolin-2-one (14) was isolated as a viscous oil (0,10g; 5,3%). M^+ 267, $^m/_z$ 163, 147, 118 and 106/105; ν_{max} ($CHCl_3$) 1690 cm^{-1}; $\delta(CDCl_3)$ 2,61 - 2,90 (4H, m), 3,09 (2H, t), 4,29 (2H, t), 6,90 - 7,19 (4H, m) and 7,28 (5H, s).
Thirdly, the parent hydroxamate (1g) (0,17g; 9,0%) identical with authentic material (n.m.r., i.r., t.l.c.) was also obtained.

Reaction of O-(2-phenylethyl) N-chloro-4-phenylbutyrohydroxamate (2h)
O-(2-Phenylethyl) N-chloro-4-phenylbutyrohydroxamate (2h) (3,35g; 0,0105 mol) silver tetrafluoroborate (2,14g; 0,011 mol) in diethyl ether (100 ml) were stirred together overnight, affording a dark brown oil (2,73g) upon work-up. Preparative t.l.c. gave N-(4-phenylbutanoyl)-3,4-dihydro-1H-2,1-benzoxazine (8) (2,35g; 79,54%) a a gum. M^+ 281, $^m/_z$ 147, 135 and 105; ν_{max} ($CHCl_3$) 1675 and 1395 cm^{-1}; $\delta(CDCl_3)$ 1,80 - 2,26 (2H, m), 2,41 - 2,78 (4H, m), 2,90 (2H, t), 4,17 (2H, t), 6,85 - 7,30 (3H, m), 7,19 (5H, s) and 7,86 - 8,05 (1H, m) and N-(2-phenylethoxy)-1,3,4,5-tetrahydro-2H-benzazepin-2-one (15) (0,21g; 7,06%). M^+ 281, $^m/_z$ 176, 161, 132 and 105; ν_{max} ($CHCl_3$) 1675 and 1390 cm^{-1}; $\delta(CDCl_3)$ 2,10 - 2,31 (4H, m) 2,58 - 2,79 (2H, m), 2,98 (2H, t), 4,17 (2H, t), 7,05 - 7,25 (4H, m) and 7,18 (5H, s).

Reaction of O-(3-phenyl-1-propyl) N-chloro-3-phenylpropanohydroxamate (2i)
O-(3-Phenyl-1-propyl) N-chloro-3-phenylpropanohydroxamate (2i) (3,23g,0,0102 mol) and silver tetrafluoroborate (1,98g 0,0102 mol) in diethyl ether (100 ml), were stirred overnight affording a dark brown oil (2,36g). Preparative t.l.c. gave N-(3-phenylpropoxy)-3,4-dihydro-1H-quinolin-2-one (16) (0,75 g; 26,1%, as a viscous oil. M^+ 281, $^m/_z$ 163, 147 and 119/118; ν_{max} ($CHCl_3$) 1690 cm^{-1}; $\delta(CDCl_3)$ 1,80 - 2,30 (2H, m), 2,49 - 2,93 (6H, m), 4,03 (2H, t), 6,99 - 7,15 (4H, m) and 7,18 (5H, s). The parent hydroxamate (1i) (0,5g; 17,3%) identical with authentic material (n.m.r., i.r., t.l.c.), was also isolated.

Reaction of O-(3-phenyl-1-propyl) N-chloro-4-phenylbutyrodhydroxamate (2j)
An ether solution (100 ml) of O-(3-phenyl-1-propyl) N-chloro-4-phenylbutyro-hydroxamate (2j) (1,39g; 4,2 mmol) was stirred overnight with silver tetrafluoroborate (0,82g; 4,2 mmol), giving a brown oil (1,09g) upon work-up. Preparative t.l.c. gave 3'-phenyl-1'-propyl 4-phenylbutyrate (33) (0,10g; 8,4%) by comparison with authentic material (n.m.r., i.r., analytical h.p.l.c.), N-(3-phenyl-1-propoxy)-1,3,4,5-tetrahydro-2H-benzazepin-2-one (17) (0,43g; 34,66%), as a gum. M^+ 295, $^m/_z$ 191, 177, 161, 149, 132 and 106; ν_{max} ($CHCl_3$) 1675 cm^{-1}; $\delta(CDCl_3)$ 1,70 - 2,90 (6H, m), 2,51 - 2,90 (4H, m), 3,96 (2H, t), 7,10 - 7,40 (4H, m) and 7,15 (5H, s) and parent hydroxamate (1j) (0,14g; 11,21%) identical with authentic material (n.m.r., i.r., t.l.c.).

Reaction of O-methyl N-chlorophenylacetohydroxamate (2l)
An ether solution (100 ml) of O-methyl N-chlorophenylacetohydroxamate (2l) (2,0g; 10,0 mmol) containing silver tetrafluoroborate (2,1g 11,0 mmol) was stirred overnight affording a dark brown gum (1,2g) after work-up. Preparative t.l.c. and recrystallisation from benzene-petroleum ether gave N-methoxy-2,3-dihydro-1-indol-2-one (11) (0,40g; 24,51%) m.p. 84°C (lit. m.p.[2] 84 - 86°C). M^+ 163, $^m/_z$ 148, 132, 120, 104, 92 and 77; ν_{max} ($CHCl_3$) 1730 and 1375 cm^{-1}; $\delta(CDCl_3)$ 3,43 (2H, s), 3,99 (3H, s) and 6,88 - 7,39 (4H, m). (Found: C 66,0; H 5,5; N 8,6%. $C_9H_9NO_2$ requires C 66,25; H 5,56; N 8,58%).

Reaction of O-methyl N-chloro-3-phenylpropanohydroxamate (2m)
(i) in diethyl ether-benzene solution
A solution of O-methyl N-chloro-3-phenylpropanohydroxamate (2m) (2,39g; 11,2 mmol) in a mixture of diethyl ether and benzene (1:1; 50 ml) was stirred overnight with silver tetrafluoroborate) (2,18g; 11,2 mmol). Work-up and preparative t.l.c. afforded after recrystallisation from benzene-petroleum ether, O-methyl N-phenyl-3-phenylpropanohydroxamate (30) m.p. 64 - 66°C. M^+ 255, $^m/_z$ 123, 105, 91 and 77; ν_{max} ($CHCl_3$) 1680, 1500 and 1380 cm^{-1}; $\delta(CDCl_3)$ 2,78 - 3,03 (4H, m) 3,55 (3H, s) 7,21 (5H, s) and 7,20 - 7,48 (5H, m). (Found: C 75,4; H 6,8; N 5,4%. $C_{16}H_{17}NO_2$ requires C 75,27; H 6,71; N 5,49%). A second component isolated as a viscous oil (0,8g) was distilled to give N-methoxy-3,4-dihydro-1H-quinolin-2-one (12) (40%) b.p. 140°C at 0,75 mm Hg. M^+ 177, $^m/_z$ 162, 147, 118 and 77; ν_{max} ($CHCl_3$) 1690 cm^{-1}; δ ($CDCl_3$) 2,43 - 3,04 (4H, m), 3,87 (3H, s) and 7,05 - 7,35 (4H, m).
(ii) in diethyl ether-tetrahydrofuran solution
In a similar reaction, a solution of O-methyl N-chloro-3-phenylpropanohydrox-amate (2m) (0,62g; 2,9 mmol) in a 1:1 mixture of diethyl ether-tetrahydrofuran (50 ml) was stirred for three hours with silver tetrafluoroborate (0,68g; 3,4 mmol). Work-up afforded a brown oil (0,76g) which upon preparative t.l.c. gave N-methoxy-3,4-dihydro-1H-quinolin-2-one (12) (0,29g; 55,14%). N.m.r. spectra of the remaining components revealed trace amounts of the parent hydroxamate (1m) and other unidentified minor components.

Reaction of O-methyl N-chloro-4-phenylbutyrohydroxamate (2n)

(i) in diethyl ether–benzene solution

A solution of O-methyl N-chloro-4-phenylbutyrohydroxamate (2n) (1,77g; 7,8 mmol) in 1:1 diethyl ether–benzene mixture (50 ml) was stirred overnight with silver tetrafluoroborate (1,51g; 7,8 mmol). Work-up and preparative t.l.c. gave O-methyl N-phenyl-4-phenylbutyrohydroxamate (31) (0,61g; 29%), b.p_1 170°C at 0,3 mm Hg. M^+ 269, m/z 239, 147, 129, 123 and 77; ν_{max} ($CHCl_3$) 1675 and 1385 cm^{-1}; δ($CDCl_3$) 1,79 - 2,24 (2H, m), 2,36 - 2,83 (4H, m), 3,59 (3H, s), 7,22 (5H, s) and 7,25 - 7,55 (5H, m). (Found: C 75,5; H 7,1; N 5,25%. $C_{17}H_{19}NO_2$ requires C 75,81; H 7,11; N 5,20%.)

A second component was isolated as a viscous oil (0,61g), which upon distillation afforded N-methoxy-1,3,4,5-tetrahydro-2H-benzazepin-2-one (13) (41%) b.p. 145°C at 0,5 mm Hg. M^+ 191, m/z 160, 147, 132, 123 and 91; ν_{max} ($CHCl_3$) 1671 cm^{-1}; δ($CDCl_3$) 2,10 - 2,35 (4H, m), 2,60 - 2,91 (2H, t), 3,74 (3H, s), 7,14 - 7,41 (4H, m). (Found: C 68,6; H 6,7; N 7,25%. $C_{11}H_{13}NO_2$ requires C 69,09; H 6,85; N 7,32%).

(ii) in diethyl ether–tetrahydrofuran solution

In a similar reaction conducted in a 1:1 mixture of diethyl ether and tetrahydrofuran and stirred for three hours, the N-methoxy-1,3,4,5-tetrahydro-2H-benzazepin-2-one (13) (n.m.r., i.r., t.l.c.) was produced in 58,4% yield together with minor unidentifiable products.

Reaction of O-methyl N-chloro-(p-methoxyphenyl)acetohydroxamate (2o)

A solution of O-methyl N-chloro-(p-methoxyphenyl)acetohydroxamate (2o) (1,03g; 4,5 mmol) in diethyl ether (50 ml) was stirred overnight with silver tetrafluoroborate (1,0g; 5,1 mmol). Work-up and preparative t.l.c. gave N-methoxy-1-azaspiro[3,5]-nona-5,8-diene-2,7-dione (20) (0,08g; 9,9%). M^+ 179 (weak), m/z 148, 137, 121 and 106; ν_{max} ($CHCl_3$) 1790 and 1680 cm^{-1}; δ ($CDCl_3$) 2,95 (2H, s), 3,80 (3H, s), 6,48 and 6,95 (4H, 2xd, J 9,33 Hz), N-methoxy methoxy-2,3-dihydro-1-indol-2-one (25) (0,02g; 2,3%) isolated as a viscous oil. M^+ 193, m/z 162, 150, 122 and 91; ν_{max} ($CHCl_3$) 1720 and 1390 cm^{-1}; δ ($CDCl_3$) 3,49 (2H, s), 3,79 (3H, s) 4,01 (3H, s) and 6,83 (3H, s) and, after recrystallisation from benzene-petroleum ether, chloro-N-methoxy methoxy-2,3-dihydro-1-indol-2-one (26) (0,11g; 10.74%), m.p. 176 - 178°C. M^+ 227, m/z 196, 184 and 169; ν_{max} ($CHCl_3$) 1730 and 1635 cm^{-1}; δ(60 MHz; $CDCl_3$) 3,40 (2H, s), 3,87 (3H, s), 3,97 (3H, s), 6,58 (1H, broad s) and 7,20 (1H, broad s). A number of minor unidentifiable components were also obtained.

Reaction of O-methyl N-chloro-3-(p-methoxyphenyl)propanohydroxamate (2p)

A mixture of O-methyl N-chloro-3-(p-methoxyphenyl)propanohydroxamate (2p) (3,07g; 0,0126 mol) and siler tetrafluoroborate (2,45g; 0,0126 mol) in diethyl ether (100 ml) was stirred overnight to yield after work-up and preparative t.l.c. the N-methoxy-6-methoxy-3,4-dihydro-1H-quinolin-2-one (24) (0,33g; 12,64%) as a viscous oil, M^+ 207, m/z 176, 149, 133 and 104; ν_{max} ($CHCl_3$) 1680 and 1380 cm^{-1}; δ(500 MHz; $CDCl_3$) 2.65 (2H,t), 2.86 (2H, t), 3.78 (3H, s) 3,88 (3H, s), 6,71 (1H, d, J=2.6Hz), 6.78 (1H, dd, J=8,7 and 2,7Hz) and 7,11 (1H, d, J=8.8Hz), after recrystallisation from benzene-petroleum ether, N-methoxy-1-azaspiro [4,5]deca-6,9-diene-2,8-dione (21) (9,04%) m.p. 125 - 127°C. M^+ 193, m/z 163, 135, 106 and 91; ν_{max} ($CHCl_3$) 1725 and 1680 cm^{-1}; δ($CDCl_3$) 2,10 - 2,71 (4H, m), 3,77 (3H, s), 6,33 and 6,82 (4H, 2xd, J 10,33 Hz). (Found: C 61,65; H 5,8; N 7,1%. $C_{10}H_{11}NO_3$ requires C 62,17; H 5,74; N 7,25%) and parent O-methyl 3-(p-methoxyphenyl)propanohydroxamate (1p) (0,74g; 28,07%) identical with authentic material (n.m.r., i.r., t.l.c.).

Reaction of O-methyl N-chloro-4-(p-methoxyphenyl)butyrohydroxamate (2q)

An ether solution (100 ml) of O-methyl N-chloro-4-(p-methoxyphenyl)butyro-hydroxamate (2q) (2,10g; 8,1 mmol) was stirred overnight with silver tetrafluoroborate (1,75g; 9,0 mmol) to give a dark brown gum (1,83g) which upon preparative t.l.c. and recrystallisation from benzene-petroleum ether afforded N-methoxy-1-azaspiro[5,5]undeca-7,10-diene-2,9-dione (22) (51,83%) m.p. 104,5 - 106°C. M^+ 207, m/z 177, 149, 133, 91 and 78; ν_{max} ($CHCl_3$) 1675, 1635 and 1340 cm^{-1}; δ($CDCl_3$) 1,83 - 2,14 (4H, m), 2,40 - 2,69 (2H, t), 3,71 (3H, s), 6,32 and 7,04 (4H, 2xd, J 9,33 Hz). (Found: C 63,75; H 6,2; N 6,75%. $C_{11}H_{13}NO_3$ requires C 63,76; H 6,32; N 6,76%). No other identifiable products could be isolated from the reaction mixture.

Reaction of O-methyl N-chlorobenzohydroxamate (2k)

(i) in the presence of benzene

O-Methyl N-chlorobenzohydroxamate (2k) (1,22g; 6,6 mmol) in a mixture of diethyl ether (40 ml) and benzene (30 ml) was stirred overnight with silver tetrafluoroborate (1,28g; 7,0 mmol). Work-up and preparative t.l.c. gave O-methyl N-phenylbenzohydroxamate (29) (0,74g; 49,34%) as a low-melting solid, which was distilled, b.p_1 164°C at 0,7 mm Hg. M^+ 227, m/z 197, 122 (trace), 105 and 177; ν_{max} ($CHCl_3$) 1665 and 1360 cm^{-1}; δ($CDCl_3$) 3,64 (3H, s) and 7,15 - 7,74 (10H, m). (Found: C 74,2; H 5,75; N 6,1%. $C_{14}H_{13}NO_2$ requires C 73,99; H 5,77; N 6,16%). Parent hydroxamate (1k) (0,07g; 6,4%) was also isolated.

(ii) in the presence of toluene

In a similar reaction to the above, O-methyl N-chlorobenzohydroxamate (2k) (2,0g; 0,0107 mol) in diethyl ether (100 ml) containing toluene (10 ml) was stirred overnight with silver tetrafluoroborate (2,0g; 0,0103 mol). Work-up and preparative t.l.c. gave O-methyl N-(p-tolyl)benzohydroxamate (27) (0,63g; 24,40%) as a viscous oil. M^+ 241, m/z 105, 77 and 51. ν_{max} ($CHCl_3$) 1660 and 1360 cm^{-1}; δ(60 MHz; $CDCl_3$), 2,25 (3H, s), 3,58 (3H, s), 7,0 - 7,38 (7H, m) and 7,40 - 7,65 (2H, m). (Found: C 74,4; H 6,4; N 5,85%. $C_{15}H_{15}NO_2$ requires C 74,67; H 6,27; N 5,81%). O-methyl N-(o-tolyl)benzohydroxamate (28) was also isolated as a viscous oil (0,52g; 20,15%). M^+ 241, m/z 105, 77 and 51. ν_{max} ($CHCl_3$) 1660 and 1360 cm^{-1}; δ(60 MHz; $CDCl_3$) 2,24 (3H, s), 3,58 (3H, s), 7,05 - 7,35 (7H, m) and 7,40 - 7,65 (2H, m). (Found: C 74.8; H 6,3; N 5,8%. $C_{15}H_{15}NO_2$ requires C 74,67; H 6,27; N 5,81%).

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