Rearrangement of *N*-acyl-3,4-dihydro-1*H*-2,1-benzoxazines to 2-substituted-4*H*-3,1-benzoxazines through a retro-Diels–Alder extrusion of formaldehyde

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***N*-Acyl-3,4-dihydro-1*H*-2,1-benzoxazines (3) undergo a thermal decomposition involving loss of formaldehyde in a retro-Diels–Alder reaction. The resultant *N*-acylazaxylylenes† (4) undergo a 6π electrocyclisation to give 2-substituted-4*H*-3,1-benzoxazines (5) rather than a 4π electrocyclisation to give the *N*-acyl-1,2-dihydrobenzazetes (6). Compounds 5 have been fully characterised spectroscopically and their data is inconsistent with that reported previously by other workers for what are purported to be the same compounds. 2-Methyl-4*H*-3,1-benzoxazine (5b) and other 2-alkyl-substituted compounds undergo facile hydrolysis to *o*-aminobenzyl esters (9) which rearrange to the thermodynamically more stable *o*-hydroxymethylanilides (10). 2-Phenyl-4*H*-3,1-benzoxazine (5a) is relatively stable to hydrolysis but undergoes a novel photochemical ring opening (> 254 nm) to give the *N*-benzoylazaxylylene (12) which can be trapped with alcohols giving *o'*-alkoxymethylbenzanilides (11). In cyclohexanol at 160 °C, the intermediate in the thermal rearrangement of 3a to 5a, *N*-benzoylazaxylylene (12), was trapped as *o'*-cyclohexyloxymethylbenzanilide (11b). The rearrangements in mesitylene are unimolecular with activation energies of 35, 37 and 42 kcal mol^{-1}‡ for 3a, 3c and 3d, respectively. The extrusion and electrocyclisation reaction pathways for *N*-acetyl-3,4-dihydro-2,1-benzoxazine (3b) have been modelled using AM1 molecular orbital theory which predicts both a non-synchronous transition state for the retro-Diels–Alder reaction and the preferred mode of ring closure to be the 6π rather than the 4π electrocyclisation.**

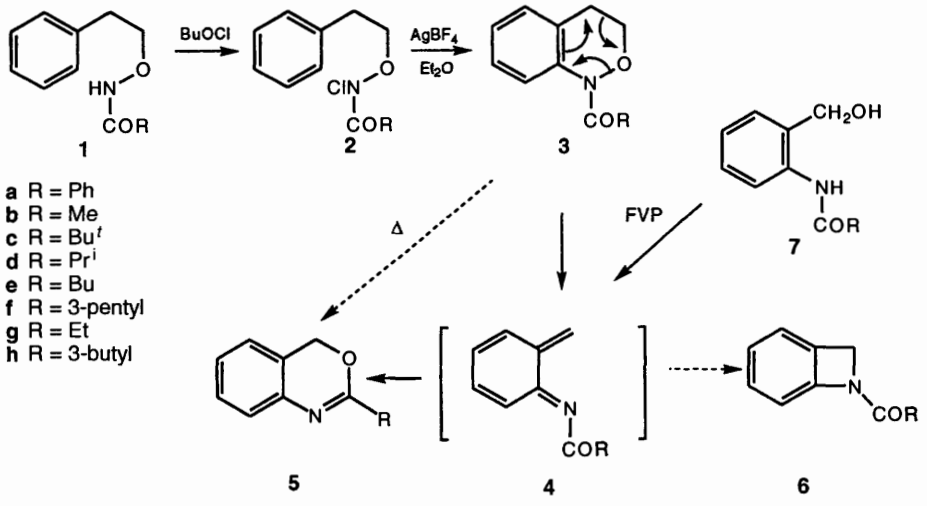
2,1-Benzoxazines are novel members of the benzoxazine family; while most other benzoxazine configurations are known,[1] the synthesis of 3,4-dihydro-1*H*-2,1-benzoxazines (3) from the cyclisation of *N*-alkoxynitrenium ions (Scheme 1) was described only quite recently.[2–4] The parent 1*H*-2,1-benzoxazine has not yet been reported in the literature and in view of this we attempted to dehydrogenate *N*-phenyl-3,4-dihydro-1*H*-2,1-benzoxazine (**3a**) by heating in a melt with sulfur. The ^{1}H NMR spectrum of the resultant product mixture displayed a four spin aromatic system between δ 6.98 and 7.40, a two proton singlet at δ 5.36 and only one aliphatic carbon at δ 66.05 in the ^{13}C NMR spectrum. In addition, the reaction evolved formaldehyde. Heating to its melting point of 149–151 °C in an oil bath or over a low flame without sulfur resulted in a clean conversion to the same compound. Formaldehyde evolved in the reaction was identified as such by the formation of formaldehyde 2,4-dinitrophenylhydrazone when the reaction was repeated under a stream of nitrogen gas which was passed through methanolic 2,4-dinitrophenylhydrazine. Decomposition of **3a** was thus shown to proceed by extrusion of formaldehyde.

A molecular ion of *m/z* 209 in its mass spectrum and microanalysis of the recrystallised product accorded the structure with molecular formula $C_{14}H_{11}NO$. *N*-Benzoyl-1,2-dihydrobenzazete (**6a**), 2-phenyl-4*H*-3,1-benzoxazine (**5a**) and the *N*-benzoylazaxylylene (**4a**) are possible products. The aliphatic nature of the methylene carbon as well as the singlet nature of the 2-proton resonance at δ 5.36 rules out the azaxylylene **4a** as the product. In addition, according to literature reports, **4a** would be expected to cyclise rapidly to either **5a** or **6a**; *N*-phenyl- and *N*-methyl-1,2-dihydrobenzazetes have been synthesised *via* the corresponding azaxylylenes by extrusion of sulfur dioxide from benzosultams.[5] Recently Sander and Morawietz isolated 1,2-dihydrobenzazete by photolysis of (*o*-aminophenyl)-diazomethane or flash vacuum pyrolysis of *o*-aminobenzyl-alcohol.[6] In the latter cases, evidence presented indicated that precursors were the azaxylylenes which cyclised thermally or photochemically to 1,2-dihydrobenzazetes. Burgess and McCullagh earlier reported a rapid reversible thermal or photochemical equilibrium between *N*-phenyl-1,2-dihydrobenzazete and *N*-phenylazaxylylene.[7] Storr and co-workers have however reported that FVP of *o*-hydroxymethylanilides at 750 °C produces not the *N*-acyl-1,2-dihydrobenzazete but rather 2-substituted-3,1-benzoxazines. Both 2-phenyl- and 2-methyl-4*H*-3,1-benzoxazines (**5a**) and (**5b**) were products from decomposition of the anilides **7a** and **7b**, however the characterisation of the products was not reported. They contended that *N*-acylazaxylylenes do not normally cyclise to 1,2-dihydrobenzazetes.[8]

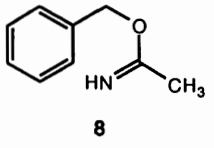
A $^3J_{CH}$ correlated 2D-NMR spectrum of the decomposition product revealed a strong correlation between the methylene protons (δ 5.4) and the carbonyl carbon (or iminyl carbon) at δ 157 which is consistent with either **5a** or **6a**. The IR spectrum indicated a strong absorption at *ca.* 1624 cm^{-1} which is in the region expected for tertiary amides or imidates while the mass spectrum showed the normal fragmentations of a benzoyl substituent (*m/z* 105, 77 and 51) as well as a strong $[M - 1]^+$ ion which is characteristic of 1,2-dihydrobenzazetes.[9] In addition, the ^{1}H NMR data of the product was inconsistent with that previously reported for 2-phenyl-4*H*-3,1-benzoxazine (**5a**).[10] However, several factors point to this, and not the 1,2-dihydrobenzazete, being the structure of the decomposition product. (*i*) 2-Phenyl-4*H*-3,1-benzoxazine has been synthesised by the dehydration of *o'*-hydroxymethylbenzanilide in

† IUPAC name for azaxylylenes is 5-imino-6-methylidenecyclohexa-1,3-diene.

‡ 1 cal = 4.184 J.



Scheme 1



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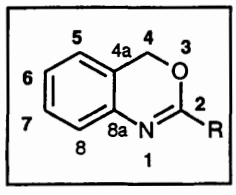
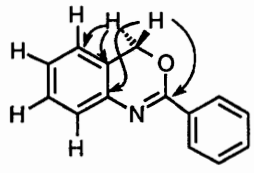




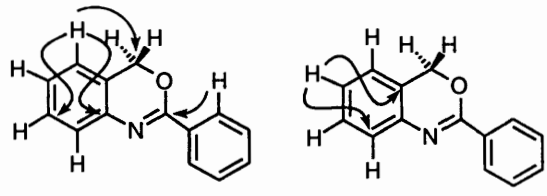


Fig. 1 Long-range CH correlations in 2-phenyl-4*H*-3,1-benzoxazine

concentrated sulfuric acid, a process which is unlikely to afford the 1,2-dihydrobenzazete.[11] It has a melting point of 90.8–92 °C which correlates with that found for our decomposition product (89–90 °C). The picrate of **5a** has a reported melting point of 170 °C, our product forms a picrate with mp 168–171 °C. The compound is soluble in dilute hydrochloric acid and is regenerated in dilute base which is unlikely to be the case for the isomeric 1,2-dihydrobenzazete. (*ii*) The IR data in the region of 1600 cm^{-1} is identical to that reported by Witkop and co-workers[11] for 2-phenyl-4*H*-3,1-benzoxazine while the λ_{max} and extinction coefficient in the UV spectrum are similar. (*iii*) While no NMR data are available for Witkop's compound, both the ^1H and ^{13}C NMR data is consistent with a 3,1-benzoxazine rather than the 1,2-dihydrobenzazete. The ring methylene protons (δ 5.34) and carbon (δ 66.45) resonate at very similar chemical shifts to the analogous protons and carbon in *O*-benzyl acetimidate (**8**, δ 5.08 and 66.92) formed from benzyl alcohol and acetonitrile by the Pinner procedure[12] and 1,2-dihydro-4*H*-3,1-benzoxazines (δ 4.8–5.4 and 65–72[13] and 4.75[10]). On the other hand the methylene resonance of *N*-benzylformamide is at δ 4.38.[14] The NMR data reported by Landor and co-workers[10] for 2-substituted-4*H*-3,1-benzoxazines is inconsistent with this configuration. The 4-methylene protons for 2-phenyl-, 2-butyl-, 2-(3-pentyl)- and 2-(2-butyl)-4*H*-3,1-benzoxazines are reported as resonating at δ 4.05, 4.22, 4.04 and 4.40, respectively, although (surprisingly) the methylene protons in the 2-isopropyl derivative resonated at a much lower field (δ 4.85). The former chemical shifts would seem to be too low for a methylene adjacent to an aromatic ring and a conjugated oxygen atom particularly in light of the shift of δ 4.75 in the dihydroprecursors.§[10] We have now synthesised the equivalent of all of these compounds as well as the 2-ethyl and 2-butyl analogues by thermal extrusion of formaldehyde from the corresponding *N*-acyl-3,4-dihydro-1*H*-2,1-benzoxazines (*vide infra*). The methylenes all resonate in the region of δ 5.1–5.3 in their ^1H NMR spectra. Furthermore, all have completely different physical and spectroscopic properties to those reported by Landor and co-workers for the same compounds.

§ The discrepancy between the methylene ^1H shifts for the benzoxazines **5a,e,f,h** and that for **5d** and between the shifts for these benzoxazines and those of their dihydro precursors was not commented upon by Landor.

We have been unable to grow suitable crystals for an X-ray analysis. However, considering the likeness of **5a** to Witkop's compound, as well as all the spectroscopic data, we conclude that the product from the thermal extrusion of formaldehyde from *N*-benzoyl-3,4-dihydro-1*H*-2,1-benzoxazine (**3a**) is the 2-phenyl-4*H*-3,1-benzoxazine (**5a**) and not the *N*-benzoyl-1,2-dihydrobenzazete (**6a**). Solvolysis reactions of 2-alkyl-4*H*-3,1-benzoxazines described below confirm this assignment.

COSY, $^1J_{CH}$ and $^3J_{CH}$ correlated 2D-NMR spectra allowed complete assignment of all ^1H and ^{13}C resonances for 2-phenyl-4*H*-3,1-benzoxazine (**5a**). In particular, a strong correlation between the benzylic methylene protons and the *ortho*-methine at δ 123.43 together with other three-bond correlations gave all the resonances in the benzoxazine ring (Fig. 1, Tables 1 and 2).

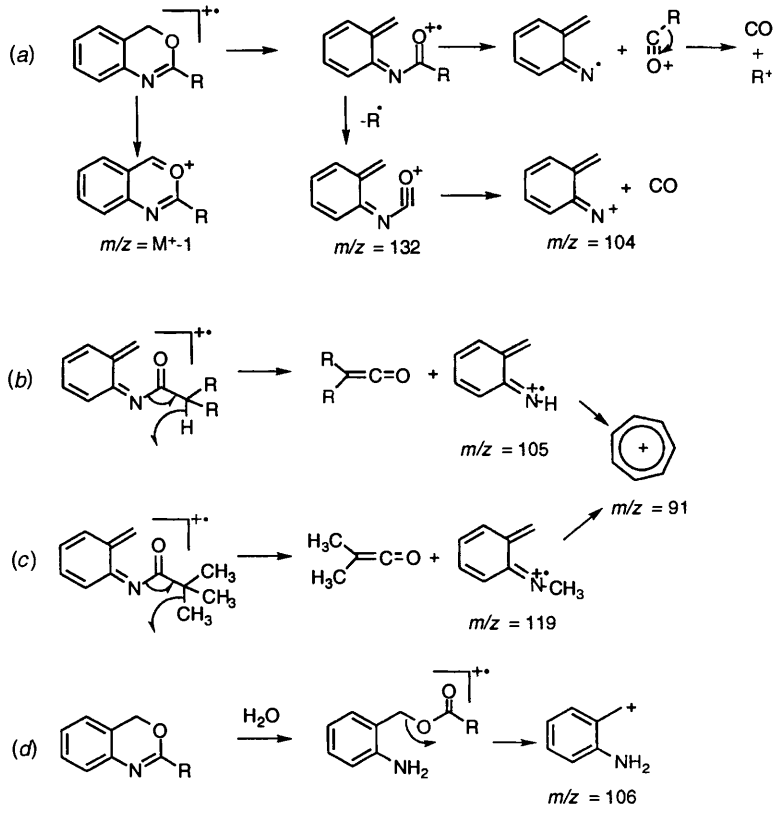
The decomposition of **3a** could also be effected cleanly in refluxing mesitylene (161 °C). Removal of solvent under reduced pressure resulted in the formation of fine white feathers of **5a**. Compounds **3c,d,g** and **h** also decomposed smoothly to give the 3,1-benzoxazines **5c,d,g** and **h** which were clear oils. However, decomposition of **3b** was best effected by heating in a Pyrex tube over a low flame to just above its melting point or in the case of **3f,g** and **h** which were liquids, heating until evolution of formaldehyde ceased. ^1H and ^{13}C NMR shifts are reported in Tables 1 and 2 and benzoxazine ^1H and ^{13}C chemical shifts were almost identical to those of **5a**. In addition, while having similar methylene ^{13}C shifts, the methyl ^1H and ^{13}C resonances for 2-methyl-4*H*-3,1-benzoxazine (δ 2.11 and 21.29, respectively) were also very similar to those found for the methyl in *O*-benzyl acetimidate (δ 1.98 and 21.96). Like **5a**, the ^1H NMR data for **5c,e,f** and **h** also differed markedly from that reported by Landor and co-workers for the products purported to be 2-isopropyl-, 2-butyl-, 2-(3-pentyl)- and 2-(2-butyl)-4*H*-3,1-

Table 1 75 MHz ^{13}C NMR data (δ, $CDCl_3$) for 2-substituted 4*H*-3,1-benzoxazines **5a–h**

R	C-4(t)	C-4a(s)	C-5(d)	C-6(d)	C-7(d)	C-8(d)	C-8a(s)	C-2(s)	Other
Ph	66.05	122.02	123.44	126.14	128.65	124.38	139.42	157.42	127.24 (d, *o*-C), 127.93 (d, *m*-C), 131.09 (d, *p*-C), 132.14 (C^i)
Me	65.99	121.41	123.59	126.20	128.91	123.79	138.64	160.97	21.29 (q, CH_3)
Bu^t	65.98	122.06	123.37	125.86	128.65	124.17	139.39	168.97	37.43 [s, $C(CH_3)_3$], 27.62 (q, 3 CH_3)
Pr^i	65.85	121.78	123.36	125.86	128.61	123.89	138.99	167.16	34.11 (d, CH), 19.52 (q, 2 CH_3)
Butyl	65.88	121.66	123.53	126.06	128.80	123.83	138.93	163.98	34.82 (t, C-1′), 28.45 (t, C-2′), 22.34 (t, C-3′) and 13.75 (q, C-4′)
3-Pentyl	65.79	122.04	123.56	126.02	128.83	123.96	139.04	166.06	49.43 (d, CH), 25.63 (t, CH_2) and 12.05 (q, CH_3)
Ethyl	65.89	121.65	123.47	126.01	128.73	123.84	138.90	164.51	28.21 (t, CH_2), 10.47 (q, CH_3)
2-Butyl	65.92	121.93	123.52	126.01	128.79	123.94	139.04	166.91	41.56 (d, CH), 27.26 (t, CH_2), 17.29 (q, CH_3) and 11.73 (q, CH_3)

Table 2 300 MHz ^1H NMR data (δ, $CDCl_3$) for 2-substituted 4*H*-3,1-benzoxazines **5a–h**

R	4-H	5-H	6-H	7-H	8-H	Other
Ph	5.36 (s)	6.98 (d)	7.22 (t of d)	7.41 (t)	7.46 (d of d)	7.46–7.52 (3 H, m, *p* and *m*), 8.12 (d, *o*)
Me	5.21 (s)	6.91 (d)	7.08–7.12 (t and d, 2 H)		7.23 (t)	2.11 (3 H, s, CH_3)
Pr^i	5.18 (s)	6.90 (d)	7.10 (t)	7.12 (d)	7.26 (t)	1.23 (6 H, d, 2 CH_3), 2.59 (1 H, sept., CH)
Bu^t	5.12 (s)	6.87 (d)	7.08 (t)	7.14 (t)	7.24 (t)	1.26 (9 H, s, 3 CH_3)
Butyl	5.20 (s)	6.91 (d)	7.10–7.14 (t and d, 2 H)		7.24 (t)	2.35 (2 H, t, $COCH_2$), 1.67 (2 H, quintet, $COCH_2CH_2$), 1.42 (2 H, sextet, CH_2CH_3), 0.94 (3 H, t, CH_3)
3-Pentyl	5.19 (s)	6.93 (d)	7.10–7.15 (t and d, 2 H)		7.26 (t)	2.12 (1 H, m), 1.5–1.8 (4 H, m), 0.98 (6 H, t)
Ethyl	5.18 (s)	6.88 (d)	7.10 (t)	7.11 (d)	7.22 (t)	2.36 (2 H, q, CH_2CH_3), 1.22 (3 H, t, CH_2CH_3)
2-Butyl	5.19 (s)	6.91 (d)	7.10–7.15 (t and d, 2 H)		7.24 (t)	2.40 (1 H, sextet), 1.73 and 1.50 (2 × m, CH_2), 1.21 (d, CH_3), 0.98 (t, CH_3)



Scheme 2 Typical fragmentation pathways for *N*-acyl-4*H*-3,1-benzoxazines; (*a*) fragmentations of **5a–h**, (*b*) fragmentations of **5b** and **5d–h**, (*c*) fragmentations of **5c**, (*d*) formation of *m/z* 106 ions

benzoxazines. The structural assignments in their work must therefore be reassessed.

No mass spectral data have been reported for this class of compounds. All are characterised by an $[M - 1]^+$ ion as well as strong peaks at *m/z* 132, 106, 105 and 104. In addition, ions corresponding to the acyl side-chain were present in all the mass spectra. Plausible fragmentations are depicted in Scheme 2 and strongly suggest that under electron impact conditions, the 3,1-benzoxazines (**5**) rearrange to the azazylylenes (**4**). Loss of ketenes from the azaxylylenes would account for the strong *m/z* 105 peaks (*m/z* 119 in the case of the 2-*tert*-butyl). In addition, most subtrates showed a weak $[M^+ + 18]$ ion which accords with addition of water to the imidate. The *m/z* 106 can therefore be attributed to fragmentation of the hydrolysis products, the amino esters (*o*-aminobenzyl acetate also yields a strong *m/z* 106 ion).

All 3,1-benzoxazines except **5a** were labile compounds. Attempted purification of **5b** by centrifugal chromatography on silica gel (hexane–ethyl acetate) resulted in the isolation of two components, **9** (R = CH_3) and **10** (R = CH_3), formed by addition of water followed by *trans*-acetylation. The ^{1}H NMR spectrum of **9** has a characteristic triplet and doublet centred at δ 6.75 and 6.70, respectively, and which are attributed to the protons *p*- and *o*- to the amino substituent. Furthermore it displayed NH_2 and carbonyl stretch frequencies at 3478, 3396 and 1745 cm^{-1} in its IR spectrum. **10**, on the other hand, displays a characteristic low field aromatic doublet at δ 7.96, which is attributed to the proton *ortho* to the the amide group; through intramolecular hydrogen bonding, anilides with *o*-hydroxymethyl substituents adopt a conformation (**10**) which results in deshielding of this hydrogen by the amide carbonyl.[15] The reactant *N*-acyl-1*H*-2,1-benzoxazines (**3**) display a low field aromatic doublet in the region of δ 7.95 for a similar reason.[2,4] *o*-Hydroxymethylacetanilide also displays strong O–H, hydrogen bonded N–H and amide carbonyl absorptions at 3594, 3383 and 1683 cm^{-1} in its IR spectrum.

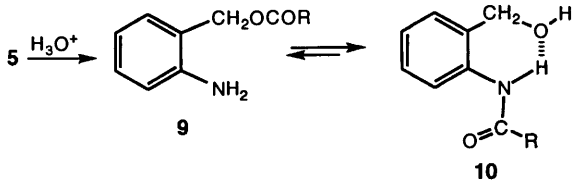
The hydrolysis of 2-methyl-4*H*-3,1-benzoxazine (**5b**) in chloroform has been reported.[8] We too have observed that **5b** undergoes hydrolysis upon stirring in aqueous acetonitrile. Analysis of extracts taken over 4 h indicated the gradual disappearance of 3,1-benzoxazine and the formation of two products, ester **9** and another which rearranged to the ester upon standing and which was likely to be the intermediate formed by the initial addition of water across the imine double bond. The ester **9** in turn rearranges slowly (over several days) to the thermodynamically more stable amide **10** upon standing at room temperature in the condensed state or in solution (Scheme 3). 2-Pivaloyl- (**5c**), 2-butyl- (**5e**), 2-(3-pentyl)- (**5f**), 2-ethyl- (**5g**) and 2-(2-butyl)-benzoxazine (**5h**) were also found to hydrolyse on silica gel.

The fact that esters **9** are the initially formed products from hydrolysis is also consistent with the decomposition product being the 3,1-benzoxazine **5** rather than the 1,2-dihydrobenzazete (**6**). The latter would be expected to hydrolyse directly to the thermodynamically more stable *o*-hydroxymethylanilides (**10**). In control experiments, we have shown that (**10**) does not rearrange to (**9**) on silica gel or in the presence of acid catalyst.

The azaxylylene intermediate (**4**) could not be trapped with dienophiles. Decomposition of **3d** in mesitylene and in the presence of diethyl maleate afforded only the 3,1-oxazine (**5d**) (HPLC). Thermolysis of (**3a**) in a melt with maleic anhydride produced only the 3,1-oxazine (**4a**) as did the decomposition in neat cyclohexanone. In the latter reaction, no trace of the 3,1- or 2,1-benzoxazine, that would be formed by Diels–Alder addition to the azaxylylene, could be found by NMR analysis. The unimolecular cyclisation of azaxylylenes (**4**) to 3,1-benzoxazines (**5**) is clearly a far more facile process than intermolecular cycloaddition reactions. However, photolysis (254 nm) of 2-phenyl-4*H*-3,1-benzoxazine (**5a**) in methanol afforded an 88% yield of *o'*-methoxymethylbenzanilide (**11a**) (Scheme 4). A similar reaction mixture in the dark was unchanged over the same period. Photolysis of **5a** in neat cyclohexanol proceeded more slowly but *o'*-cyclohexyloxymethylbenzanilide (**11b**) was formed in a 66% yield. By analogy with *o*-hydroxymethylacetanilide (**10**, R = CH_3), **11a** and **11b** both displayed strong bonded NH stretch frequencies at 3360 cm^{-1} in their IR spectra as well as characteristically low field aromatic doublets for C-6'-H at δ 8.41 in their ^{1}H NMR spectra due to anisotropic deshielding by the carbonyl. Both must be generated by addition of the alcohol to the azaxylylene formed by photochemical conrotatory ring opening. This interception of azaxylylenes by mildly nucleophilic alcohols such as methanol and cyclohexanol is attributed not only to the large excess of alcohol but also to the nature of the ground state azaxylylene which is predicted to be strongly dipolar. The positive character of the methylidine carbon would be reinforced by both the electronegative nitrogen atom in the 4-position as well as the −M effect of the *N*-acyl substituent (**12**, Scheme 4). 2-Phenyl-4*H*-3,1-benzoxazine (**5a**) was recovered unchanged after several hours of irradiation in anhydrous ether thus confirming that photochemical or thermal ring closure of **4a** to **5a** must be extremely rapid at ambient temperature.

The intermediacy of the azaxylylene (**4a**) in the thermal extrusion of formaldehyde by *N*-benzoylbenzoxazine (**3a**) was demonstrated through its decomposition in neat cyclohexanol (bp 160 °C). The reaction afforded a mixture of 2-phenyl-4*H*-3,1-benzoxazine (**5a**, 83%) as well as **11b** (12.5%). 2-Phenyl-4*H*-3,1-benzoxazine is stable in cyclohexanol at this temperature. Thermolysis of 2,1-benzoxazines therefore proceeds by a retro-Diels–Alder reaction yielding the azaxylylene intermediate which is extremely reactive and cyclises at these temperatures to the 3,1-benzoxazine rather than to the 1,2-dihydrobenzazete.

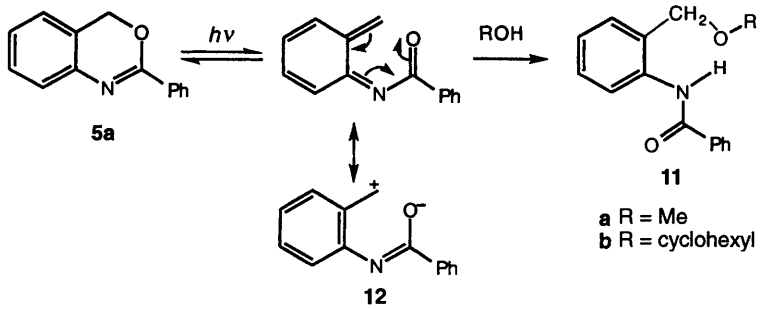
Clearly thermal *E–Z* isomerism about the azaxylylene imine bond, a process necessary for intramolecular cyclisation to the 3,1-benzoxazine, is readily achieved at the temperatures of these studies. Such isomerisations are known though to be relatively low energy processes.[16] Our results concur with those of Storr and co-workers who found that *N*-acylazaxylylenes, formed by thermal dehydration of *o*-hydroxymethylanilides in FVP experiments, also afforded 3,1-benzoxazines.[8]



Scheme 3

AM1 calculations

AM1 semiempirical molecular orbital calculations support these studies. Extrusion of formaldehyde from *N*-acetylbenzoxazine (**3b**) involves a concerted breaking of both the C–C and the N–O bonds. The potential energy surface for the reaction is depicted in Fig. 2. The gas phase activation barrier is significant (56 kcal mol^{-1}) and the overall process is predicted to be slightly endothermic (Fig. 3). In the transition state (Fig. 2) the N–O



Scheme 4

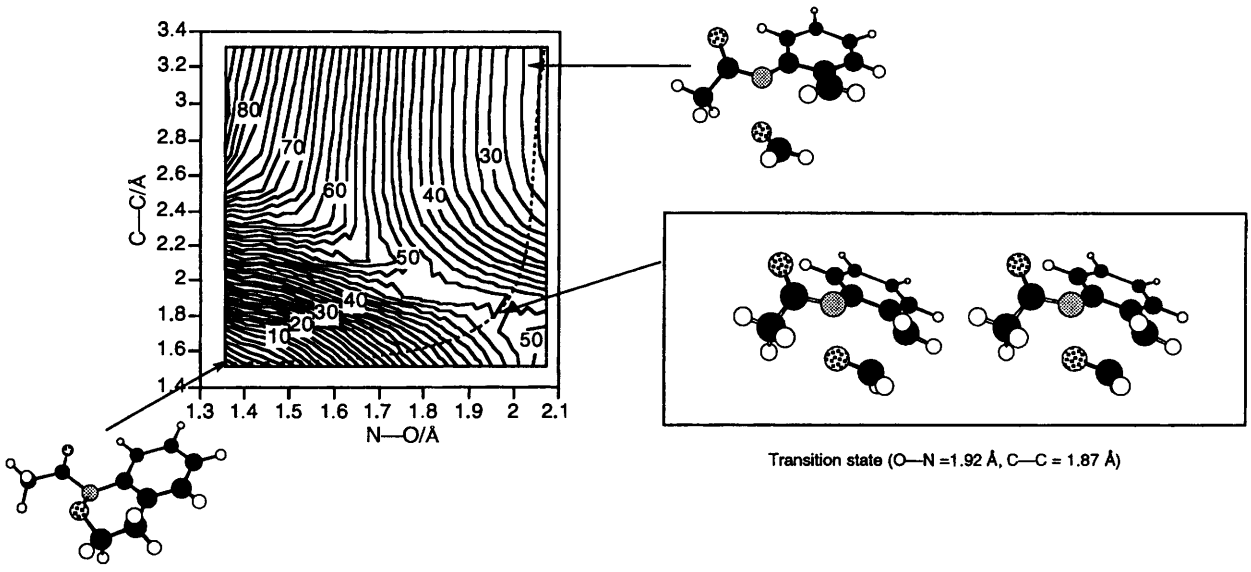


Fig. 2 Reaction surface and transition state (inset) for the extrusion of formaldehyde from *N*-acetyl-3,4-dihydro-1*H*-2,1-benzoxazine (**3b**)

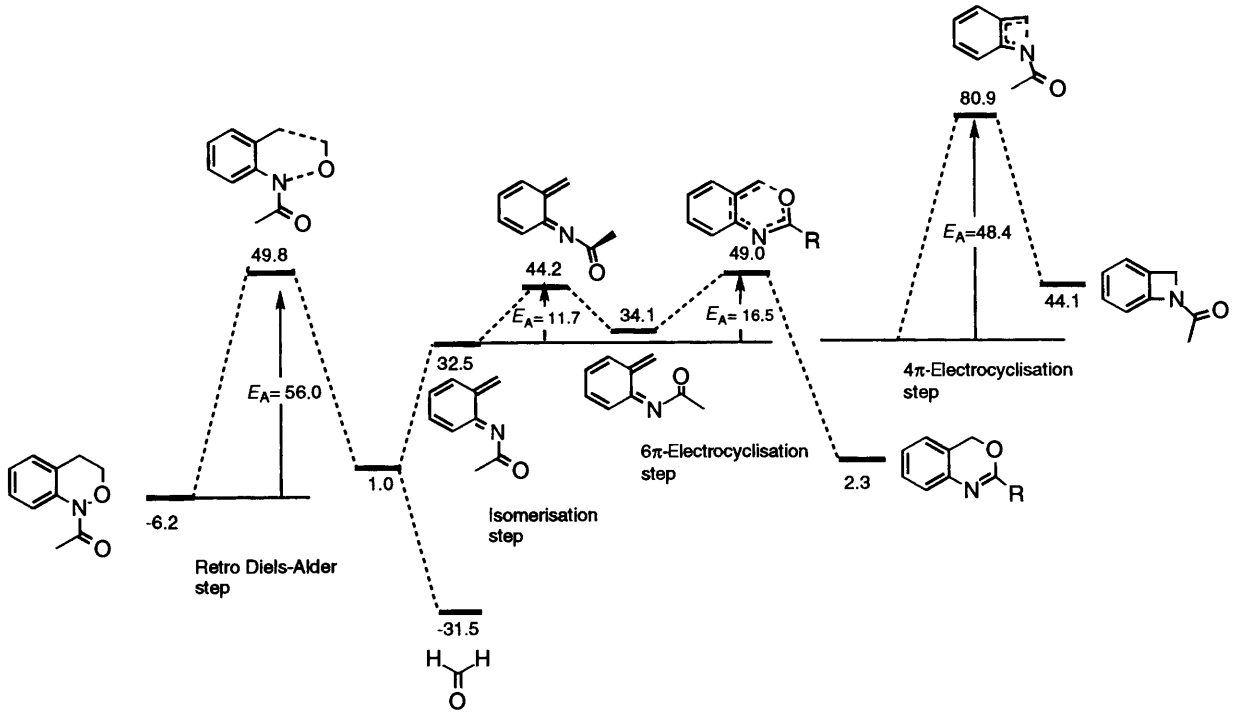


Fig. 3 Gas phase AM1 heats of formation (kcal mol^{-1}) along the reaction coordinate for the extrusion of formaldehyde from *N*-acetyl-3,4-dihydro-1*H*-2,1-benzoxazine (**3b**) and the cyclisation of azaxylylene (**4b**) to 2-methyl-4*H*-3,1-benzoxazine (**5b**) and *N*-acetyl-1,2-dihydrobenzazete (**6b**)

bond (1.92 Å) is slightly longer than the C–C bond (1.87 Å) which indicates a non-synchronous process since X-ray data (N–O, 1.41 and C–C, 1.51 Å[17]) and the AM1 optimised geometry (N–O, 1.35 and C–C, 1.52 Å) predict the N–O bond to be significantly shorter (*ca.* 0.1 Å) than the C–C bond in the parent 2,1-benzoxazine. Although these preliminary semiempirical results must be treated with a degree of caution,¶ this tighter binding between the C–C bonds in the transition state is readily rationalised using Frontier Orbital Theory.[21] The relative energies of the azaxylylene and formaldehyde frontier orbitals

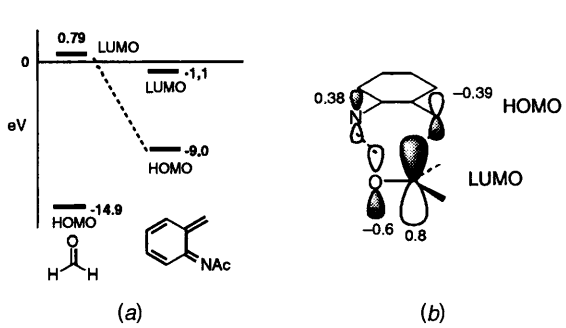


Fig. 4 (*a*) HOMO–LUMO energetics and (*b*) HOMO–LUMO coefficients for the extrusion of formaldehyde from *N*-acetyl-3,4-dihydro-1*H*-2,1-benzoxazine (**3b**)

suggest a stronger interaction between the LUMO of formaldehyde and the HOMO of the azazylylene (Fig. 4). N and C coefficients in the latter are almost identical (0.38 for N

¶ AM1 results for NO-containing systems, while being measurably better than those obtained using the earlier MNDO method, are reported to give less accurate results than those for hydrocarbons.[18] Our calculations on the properties of O,N containing alkoxynitrenium ions,[19] HERON rearrangements and anomeric effects of *N*-heteroatom-substituted *N*-alkoxyamides[20] suggest that the semi-empirical methods reproduce *ab initio* properties of N,O-containing systems quite well.

and −0.39 for C) however the C and O coefficients in the LUMO of formaldehyde are 0.8 and −0.6, respectively. A stronger overlap would thus be expected between the C–C terminal atoms in the transition state.

Inversion at the imine nitrogen requires only *ca.* 12 kcal mol^{-1} in line with experimental barriers for imines substituted at nitrogen with electron-withdrawing groups[16] and the process of electrocyclisation to the 3,1-benzoxazine is predicted to be favourable in the gas phase, being both exothermic and of low activation enthalpy (only 16.5 kcal mol^{-1}). While this barrier is considerably less than that for the retro-Diels–Alder step, it would be expected to be lowered further in the solution state.[20] Cyclisation of the azaxylylene to the 1,2-dihydrobenzazete is by comparison an extremely high energy pathway and the reaction is endothermic by *ca.* 12 kcal mol^{-1}. This is consistent with the formation of a highly strained fused four-membered ring. The full profiles for decomposition of **3b** and cyclisations of **4b** are depicted in Fig. 3.

Reaction kinetics

The decomposition of *N*-benzoyl-, *N*-pivaloyl- and *N*-(2-methylpropanoyl)-2,1-benzoxazines follow clean unimolecular kinetics in mesitylene. The *N*-acetyl-2,1-benzoxazine transformed at a much lower rate and decomposition products from 3,1-benzoxazine interfered with HPLC analysis; hence a kinetic investigation was precluded. Arrhenius plots are depicted in Fig. 5.

Activation energies for *N*-benzoyl-, *N*-pivaloyl- and *N*-isopropyl-2,1-benzoxazines are significant while entropies of activation are mildly positive in accord with there being fewer steric constraints in the transition states than in the reactants (Table 3). Interestingly, *N*-pivaloyl-2,1-benzoxazine has a tighter transition state than the other two we have studied. An increase in imine character at the nitrogen atom would account for this; part of the positive entropy change is offset through an increased steric effect as the *N*-acyl group becomes co-planar with the aromatic ring.

The experimental barriers are lower than the theoretical one predicted by AM1 for the decomposition of *N*-acetyl-2,1-benzoxazine in the gas phase. This activation enthalpy would however be expected to be significantly smaller in the solution state owing to the dipolar nature of the transition state and products, azaxylylene and formaldehyde.

Experimental

Melting points were determined on a Reichert Microscopic Hot-Stage and are uncorrected. IR spectra were recorded on a Perkin Elmer 1725 × FT instrument. 300 MHz ^{1}H and 75 MHz ^{13}C NMR spectra were recorded on a Bruker AC-300P FT spectrometer. HPLC analyses were performed on a Waters 510 analytical instrument using a model 481 UV absorbance detector linked to a Waters 740 data module. Acetonitrile used was HiPerSolv, 'Far UV' grade (BDH). Mass spectral data were obtained on a Kratos MS902 spectrometer through the Mass Spectroscopy Unit of Sydney University. Microanalytical data was obtained from The Research School of Chemistry at Canberra. Flash chromatography was executed on columns loaded with Kieselgel 60 (Merck). Centrifugal chromatography was carried out on a Harrison Research Chromatotron Model 7924T. Deuteriated acetonitrile (CD_3CN), 99.5%, was purchased from Aldrich. Anhydrous sodium sulfate or calcium chloride was used for drying all organic mixtures. Ether refers to anhydrous diethyl ether stored over sodium wire. ^{1}H and ^{13}C NMR designations are: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet). AM1 calculations were executed on a DEC 5000 workstation using MOPAC.[18,22] Force calculations were run on all calculated geometries of reactants and products to ensure that they corresponded to minima on the the potential energy surface (all real force constants). The approximate transition state for the extrusion of formaldehyde from *N*-acetyl-1*H*-3,4-dihydro-2,1-benzoxazine was determined using a grid search in which the N–O and C^3–C^4 bonds were the reaction coordinates. The true transition state for this reaction as well as those for the electrocyclisation of the azaxylylene to 3,1-benzoxazine and 1,2-dihydrobenzazete were then refined by the TS routine within MOPAC 93. All transition structures were verified by force calculations to have exactly one imaginary force constant.

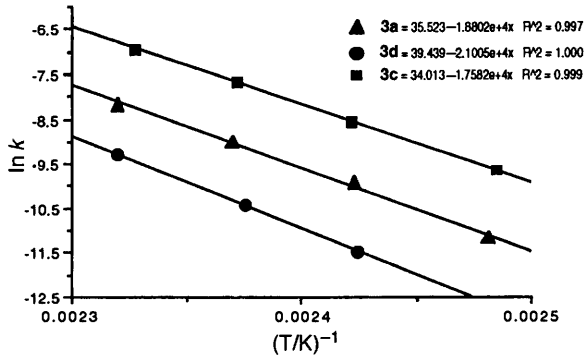


Fig. 5 Arrhenius plots for decomposition of *N*-benzoyl-, *N*-pivaloyl-, and *N*-(2-methylpropanoyl)-3,4-dihydro-1*H*-2,1-benzoxazines (**3a**,**c** and **d**) in mesitylene

Table 3 Activation energies and entropies of activation for the decomposition of *N*-benzoyl- (**3a**), *N*-pivaloyl- (**3c**) and *N*-(2-methylpropanoyl)-3,4-dihydro-1*H*-2,1-benzoxazine (**3d**) in mesitylene

	E_A/kJ mol^{-1}	E_A/kcal mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
3a	156.24 (6.2)	37.42 (1.5)	42.10 (14.8)	10.08 (3.5)
3c	146.11 (2.7)	34.99 (0.6)	29.55 (6.4)	7.08 (1.5)
3d	174.55 (3.0)	41.80 (0.7)	74.64 (7.0)	17.87 (1.7)

Synthesis of *N*-acyl-1*H*-3,4-dihydro-2,1-benzoxazines

The synthesis of *N*-benzoyl- and *N*-acetyl-1*H*-3,4-dihydro-2,1-benzoxazines (**2a**,**b**) have been described previously.[2,3] *N*-pivaloyl-, *N*-(2-methylpropanoyl)-, *N*-pentanoyl- and *N*-(2-ethylpropanoyl), *N*-propanoyl- and *N*-(2-methylbutanoyl)-1*H*-3,4-dihydro-2,1-benzoxazine (**2c**–**h**) were each synthesised from the appropriate *O*-(2-phenylethyl) hydroxamate according to the same procedures.

Synthesis of *O*-(2-phenylethyl) hydroxamates

Precursor *O*-(2-phenylethyl) hydroxamates were synthesised from potassium hydroxamates[23] and 2-phenylethyl bromide according to the procedure of Cooley *et al.*[24]

O-(2-*phenylethyl*) *pivalohydroxamate* (**1c**), prepared from the reaction of 2-phenylethyl bromide (33.3 g, 180 mmol) with potassium pivalohydroxamate (27.9 g, 180 mmol), was isolated by flash chromatography and crystallised from benzene–hexane as needles (47%), mp 102–103 °C (Found: C, 71.3; H, 9.0; N, 6.4. $C_{13}H_{19}NO_2$ requires C, 70.6; H, 8.7; N 6.3%); $\nu_{max}(CHCl_3)$/cm^{-1} 3426 (NH) and 1686 (CO); δ_H(300 MHz; $CDCl_3$) 1.15 (9 H, s, CH_3s), 2.97 (2 H, t, CH_2–Ar), 4.13 (2 H, t, CH_2–O), 7.10–7.30 (5 H, m, ArH) and 8.42 (1 H, s, NH); δ_C(75 MHz; $CDCl_3$) 27.08 (q, 3 CH_3), 34.78 (t, $ArCH_2$), 37.87 [s, $C(CH_3)_3$], 76.83 (t, CH_2–O), 126.40 (d, *p*-C), 128.48 and 128.79 (d, *m*- and *o*-C), 138.1 (s, C^i) and 176.13 (s, CO); *m*/*z* 222 (15%, M$^+$ + 1), 178 (32), 105 (73), 104 (74), 57 (100) and 41 (57).

O-(2-*Phenylethyl*) 2-*methylpropanohydroxamate* (**1d**), prepared from the reaction of 2-phenylethyl bromide (33.3 g, 180 mmol) with potassium 2-methylpropanohydroxamate (25.4 g, 180 mmol), was isolated by flash chromatography and crystallised from benzene–hexane as prisms (44%), mp 97–98 °C (Found: C, 70.5; H, 8.5; N, 6.7. $C_{12}H_{17}NO_2$ requires C,

69.6; H, 8.3; N, 6.8%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3410 and 3230 (NH) and 1685 (CO); δ_H(300 MHz; $CDCl_3$) 1.10 (6 H, d, CH_3s), 2.26 (1 H, br septet, CH), 2.95 (2 H, t, CH_2–Ar), 4.10 (2 H, t, CH_2–O), 7.10–7.37 (5 H, m, ArH) and 9.0, (1 H, s, NH); δ_C(75 MHz; $CDCl_3$) 19.13 (q, 2 CH_3), 32.13 (d, CH), 34.44 (t, CH_2Ar), 76.57 (t, CH_2–O), 126.24 (d, *p*-C), 128.32 and 128.72 (d, *m*- and *o*-C), 137.77 (s, C^i) and 175.06 (s, CO); *m*/*z* 208 (15%, M^- + 1), 105 (25), 104 (18), 91 (87), 77 (32), 65 (38), 51 (24), 43 (100), 41 (75), 39 (68) and 27 (89).

O-(2-*Phenylethyl*) *valerohydroxamate* (**1e**), prepared from the reaction of 2-phenylethyl bromide (13.9 g, 75 mmol) with potassium valerohydroxamate (11.63 g, 75 mmol), was isolated by flash chromatography and crystallised from benzene–hexane as prisms (64%), mp 82–83 °C (Found: C, 70.2; H, 8.7; N, 6.3. $C_{13}H_{19}NO_2$ requires C, 70.6; H, 8.7; N, 6.3%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3405 and 3230 (NH) and 1685 (CO); δ_H(300 MHz; $CDCl_3$; 325 K) 0.89 (3 H, t, CH_3), 1.32 (2 H, sextet, CH_2CH_3), 1.59 (2 H, t, $COCH_2CH_2$), 2.10 (2 H, br t, $COCH_2$), 2.96 (2 H, t, $ArCH_2$), 4.11 (2 H, t, CH_2–O), 7.05–7.35 (5 H, m, ArH) and 7.96 (1 H, s, NH); δ_C(75 MHz; $CDCl_3$; 325 K) 13.60 (q, CH_3), 22.32 (t, CH_2CH_3), 27.05 (br, t, $COCH_2CH_2$), 32.6 (br, t, $COCH_2$), 34.75 (t, $ArCH_2$), 126.50 (d, *p*-C), 128.56 and 128.85 (d, *m*- and *o*-C), 137.80 (s, C^i); *m*/*z* 222 (11%, M^+ + 1), 179 (33), 105 (100), 104 (96), 91 (72), 85 (74), 77 (32) and 57 (72).

O-(2-*Phenylethyl*) 2-*ethylbutyrohydroxamate* (**1f**), prepared from the reaction of 2-phenylethyl bromide (9.54 g, 52 mmol) with potassium 2-ethylbutyrohydroxamate (8.7 g, 52 mmol), was isolated by flash chromatography as a low melting solid (20%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3405 and 3230 (NH) and 1689 (CO); δ_H(300 MHz; $CDCl_3$) 0.88 (6 H, t, 2 CH_3), 1.45 (2 H, m, $CHCH_3$), 1.62 (2 H, m, $CHCH_3$), 1.90 (1 H, m, COCH), 2.95 (2 H, t, CH_2–Ar), 4.10 (2 H, t, CH_2–O) and 7.10–7.37 (5 H, m, ArH); δ_C(75 MHz; $CDCl_3$) 11.85 (q, 2 CH_3), 25.35 (t, CH_2CH_3), 34.54 (t, $ArCH_2$), 47.35 (d, COCH), 77.0 (t, CH_2–O), 126.32 (d, *p*-C), 128.39 and 128.79 (d, *m*- and *o*-C), 137.79 (s, C^i) and 173.59 (s, CO); *m*/*z* 236 (11%, M^+ + 1), 207 (15), 206 (14), 105 (100), 104 (83), 99 (34), 91 (72), 71 (58) and 43 (38) (Found *M*, 235.1522. $C_{14}H_{21}NO_2$ requires 235.1572).

O-(2-*Phenylethyl*) *propanohydroxamate* (**1g**), prepared from the reaction of 2-phenylethyl bromide (23.31 g, 126 mmol) with potassium propanohydroxamate (16 g, 23.31 mmol), was isolated by flash chromatography (54%) as a low melting solid which recrystallised from benzene–hexane, mp 49–51 °C (Found: C, 68.6; H, 8.1; N, 7.1. $C_{11}H_{15}NO_2$ requires C, 68.4; H, 7.8; N 7.3%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3401, 3244 (bonded NH) and 1693 (CO); δ_H(300 MHz; $CDCl_3$) 1.11 (3 H, br t, CH_3), 2.00–2.40 (2 H, 2 × br s, CH_2–CO), 2.95 (2 H, t, $ArCH_2$), 4.10 (2 H, br t, CH_2–O), 7.10–7.20 (5 H, m, ArH) and 8.90–9.20, (1 H, 2 × br s, NH); δ_C(75 MHz; $CDCl_3$) 9.52 (br q, CH_3), 26.25 (br t, CH_2CO), 34.50 (t, $ArCH_2$), 77.0 (br t, CH_2–O), 126.40 (d, *p*-C), 128.41 and 128.77 (d, *m*- and *o*-C), 137.77 (s, C^i) and 172.20 (s, CO); *m*/*z* 193 (12%, M^+), 164 (6), 105 (100), 104 (92), 91 (36), 57 (25) and 44 (28).

O-(2-*Phenylethyl*) 2-*methylbutyrohydroxamate* (**1h**), prepared from the reaction of 2-phenylethyl bromide (17.2 g, 93 mmol) with potassium 2-methylbutyrohydroxamate (14.4 g, 93 mmol), was isolated as a solid by flash chromatography (20%) and crystallised from benzene–hexane as needles 103–105 °C (Found: C, 70.5; H, 8.7; N, 6.1. $C_{13}H_{19}NO_2$ requires C, 70.6; H, 8.7; N 6.3%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3401, 3244 (bonded NH) and 1693 (CO); δ_H(300 MHz; $CDCl_3$) 1.11 (3 H, br t, CH_3), 2.00–2.40 (2 H, 2 × br s, CH_2–CO), 2.95 (2 H, t, $ArCH_2$), 4.10 (2 H, br t, CH_2–O), 7.10–7.20 (5 H, m, ArH) and 8.90–9.20, (1 H, 2 × br s, NH); δ_C(75 MHz; $CDCl_3$) 11.79 (q, CH_2CH_3), 17.23 (br q, $CHCH_3$), 26.92 (br t, CH_2CH_3), 34.60 (t, $ArCH_2$), 39.78 (br d, COCH), 77.0 (br t, CH_2–O), 126.44 (d, *p*-C), 128.48 and 128.83 (d, *m*- and *o*-C), 137.90 (s, C^i) and 174.42 (s, CO); *m*/*z* 221 (35%, M^+), 206 (35), 193 (46), 164 (23), 105 (93), 104 (93), 91 (78), 85 (46), 57 (100) and 41 (57).

N-Chlorination of hydroxamic esters

Hydroxamic esters in dichloromethane were converted quantitatively to their *N*-chloro derivatives by stirring with a 3 molar excess of *tert*-butyl hypochlorite at room temperature for several hours. Removal of solvent and excess *tert*-butyl hypochlorite under reduced pressure at 30 °C and in subdued light afforded the *N*-chlorohydroxamates, usually as yellow oils. The thermally labile *N*-chloro derivatives were characterised by an absence of N–H stretch and shift of the carbonyl stretch frequency to higher wavenumber in their IR spectra, as well as a characteristic downfield shift of *ca.* 0.17 ppm for the methylene protons adjacent to oxygen in their ^1H NMR spectrum and an upfield shift of *ca.* 1.5 ppm for the corresponding carbons in the ^{13}C NMR spectra.

***O*-(2-Phenylethyl) *N*-chloropivalohydroxamate (2c).** $\nu_{max}(CHCl_3)/cm^{-1}$ 1720 and 1000; δ_H(300 MHz, $CDCl_3$) 1.15 (9 H, s, $3CH_3$), 2.97 (2 H, t, $ArCH_2$), 4.30 (2 H, t, CH_2–O), 7.10–7.40 (5 H, m, ArH); δ_C(75 MHz; $CDCl_3$) 27.08 (q, 3 CH_3), 34.78 (t, $ArCH_2$), 37.86 [s, $C(CH_3)_3$], 76.83 (t, CH_2–O), 126.40 (d, *p*-C), 128.48 and 128.79 (d, *m*- and *o*-C), 138.10 (s, C^i) and 176.13 (s, CO).

***O*-(2-Phenylethyl) *N*-chloro-2-methylpropanohydroxamate (2d).** $\nu_{max}(CHCl_3)/cm^{-1}$ 1720 (CO) and 1005; δ_H(300 MHz; $CDCl_3$) 1.03 (6 H, d, CH_3s), 2.70 (1 H, septet, CH), 2.96 (2 H, t, CH_2–Ar), 4.27 (2 H, t, CH_2–O), 7.10–7.40 (5 H, m, ArH); δ_C(75 MHz; $CDCl_3$) 18.84 (q, 2 CH_3), 32.82 (d, CH), 33.76 (t, CH_2Ar), 75.86 (t, CH_2–O), 126.53 (d, *p*-C), 128.34 and 128.59 (d, *m*- and *o*-C), 137.08 (s, C^i) and 181.55 (s, CO).

***O*-(2-Phenylethyl) *N*-chlorovalerohydroxamate (2e).** $\nu_{max}(CHCl_3)/cm^{-1}$ 1739 (CO), 1603, 1497, 1466, 1454, 1145 and 1011; δ_H(300 MHz; $CDCl_3$; 325 K) 0.84 (3 H, t, CH_3), 1.21 (2 H, sextet, CH_2CH_3), 1.51 (2 H, t, $COCH_2CH_2$), 2.28 (2 H, br t, $COCH_2$), 2.97 (2 H, t, $ArCH_2$), 4.25 (2 H, t, CH_2–O) and 7.10–7.40 (5 H, m, ArH); δ_C(75 MHz; $CDCl_3$) 13.51 (q, CH_3), 21.87 (t, CH_2CH_3), 26.32 (t, $COCH_2CH_2$), 33.55 and 33.76 (t, $ArCH_2$ and $COCH_2$), 75.64 (t, CH_2–O), 126.57 (d, *p*-C), 128.40 and 128.64 (d, *m*- and *o*-C), 137.13 (s, C^i) and 178.32 (s, CO).

***O*-(2-Phenylethyl) *N*-chloro-2-ethylbutyrohydroxamate (2f).** $\nu_{max}(CHCl_3)/cm^{-1}$ 1731 (CO), 1603, 1497, 1455 and 1382; δ_H(300 MHz; $CDCl_3$) 0.77 (6 H, t, 2 CH_3), 1.39 (2 H, m, $CHCH_3$), 1.57 (2 H, m, $CHCH_3$), 2.48 (1 H, m, COCH), 2.98 (2 H, t, CH_2–Ar), 4.28 (2 H, t, CH_2–O) and 7.20–7.37 (5 H, m, ArH); δ_C(75 MHz; $CDCl_3$) 11.48 (q, 2 CH_3), 24.99 (t, CH_2CH_3), 33.86 (t, $ArCH_2$), 46.66 (d, COCH), 75.97 (t, CH_2–O), 126.63 (d, *p*-C), 128.48 and 128.70 (d, *m*- and *o*-C), 137.19 (s, C^i) and 180.54 (s, CO).

***O*-(2-Phenylethyl) *N*-chloropropanohydroxamate (2g).** $\nu_{max}(CHCl_3)/cm^{-1}$ 1744 (CO), 1603, 1497, 1455 and 1144; δ_H(300 MHz; $CDCl_3$) 1.05 (3 H, t, CH_3), 2.35 (2 H, q, CH_2–CO), 2.98 (2 H, t, $ArCH_2$), 4.25 (2 H, t, CH_2–O) and 7.10–7.30 (5 H, m, ArH); δ_C(75 MHz; $CDCl_3$) 8.57 (q, CH_3), 27.43 (t, CH_2CO), 33.79 (t, $ArCH_2$), 75.68 (br t, CH_2–O), 126.59 (d, *p*-C), 128.42 and 128.65 (d, *m*- and *o*-C), 137.04 (s, C^i) and 179.16 (s, CO).

***O*-(2-Phenylethyl) *N*-chloro-2-methylbutyrohydroxamate (2h).** $\nu_{max}(CHCl_3)/cm^{-1}$ 1730 (CO), 1603, 1497 and 1454; δ_H(300 MHz; $CDCl_3$) 0.77 (3 H, t, CH_2CH_3), 1.02 (3 H, d, $CHCH_3$), 1.03 and 1.60 (2 H, 2 × m, CH_2CH_3), 2.54 (1 H, sextet, COCH), 2.98 (2 H, t, $ArCH_2$), 4.27 (2 H, t, CH_2–O) and 7.10–7.30 (5 H, m, ArH); δ_C(75 MHz; $CDCl_3$) 11.34 (q, CH_2CH_3), 16.67 (q, $CHCH_3$), 26.67 (t, CH_2CH_3), 33.87 (t, $ArCH_2$), 39.68 (d, COCH), 75.96 (t, CH_2–O), 126.65 (d, *p*-C), 128.47 and 128.69 (d, *m*- and *o*-C), 137.19 (s, C^i) and 181.15 (s, CO).

Formation of *N*-acyl-1*H*-3,4-dihydro-2,1-benzoxazines

The *N*-chlorohydroxamic esters (typically 6–20 mmol) were reacted overnight with an equimolar quantity of silver tetrafluoroborate in anhydrous ether (50 cm^3) according to a previously reported procedure.[2,3] Silver salts were separated by filtration and washed well with chloroform. Chloroform extracts and ethereal filtrate were combined, washed with

water, dried and concentrated to give crude cyclisation mixtures which were separated by flash or centrifugal chromatography.

O-(2-Phenylethyl) *N*-chloropivalohydroxamate (**2c**) afforded, after flash chromatography, N-*pivaloyl*-3,4-*dihydro*-1H-2,1-*benzoxazine* (**3c**) (61%), which crystallised from benzene–hexane as plates, mp 65–66 °C (Found: C, 71.7; H, 8.2; N, 6.3. $C_{13}H_{17}NO_2$ requires C, 71.2; H, 7.8; N 6.4%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1651 (CO), 1488, 1456, 1396, 1345 and 1336; δ_H(300 MHz; $CDCl_3$) 1.36 (9 H, s, CH_3s), 3.04 (2 H, t, CH_2–Ar), 4.34 (2 H, t, CH_2–O), 7.05 (1 H, t, C-6-H), 7.1–7.2 (2 H, overlapping t and d, C-5-H and C-7-H, and 7.94 (1 H, d, C-8-H); δ_C(75 MHz; $CDCl_3$) 26.44 (t, $ArCH_2$), 26.77 (q, 3 CH_3), 40.02 [s, $C(CH_3)_3$], 70.62 (t, CH_2–O), 120.93 (d, C-8), 122.84 (s, C-4a), 124.01 (d, C-6), 125.69 (d, C-7), 128.60 (d, C-5), 137.31 (s, C-8a) and 175.68 (s, CO); *m*/*z* 219 (25%, M^+), 135 (100) and 57 (84).

O-(2-Phenylethyl) *N*-chloro-2-methylpropanohydroxamate (**2d**) afforded, after flash chromatography, N-2-*methylpropanoyl*-3,4-*dihydro*-1H-2,1-*benzoxazine* (**3d**) (63%) which crystallised from benzene–hexane as prisms, mp 45–46 °C (Found: C, 70.4; H, 7.7; N, 6.8. $C_{12}H_{15}NO_2$ requires C, 70.2; H, 7.4; N 6.8%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1662 (CO), 1489, 1457 and 1389; δ_H(300 MHz; $CDCl_3$) 1.20 (6 H, d, CH_3s), 2.98 (2 H, t, $ArCH_2$), 3.17 (1 H, septet, CH), 4.30 (2 H, t, CH_2–O), 7.03 (1 H, t, C-6-H), 7.08 (1 H, d, C-5-H), 7.15 (1 H, t C-7-H) and 7.96 (1 H, d, C-8-H); δ_C(75 MHz; $CDCl_3$) 18.74 (q, CH_3s), 26.42 (t, $ArCH_2$), 31.23 (d, CH), 70.69 (t, CH_2–O), 120.66 (d, C-8), 122.93 (s, C-4a), 124.18 (d, C-6), 125.88 (d, C-7), 128.60 (d, C-5), 136.54 (s, C-8a) and 175.59 (s, CO); *m*/*z* 205 (52%, M^+), 135 (97) and 43 (100).

O-(2-Phenylethyl) *N*-chlorovalerohydroxamate (**2e**) afforded pure N-*pentanoyl*-3,4-*dihydro*-1H-2,1-*benzoxazine* (**3e**) (76%) as a colourless oil; $\nu_{max}(CHCl_3)/cm^{-1}$ 1678 (CO), 1601, 1582, 1489, 1455 and 1382; δ_H(300 MHz; $CDCl_3$) 0.95 (3 H, t, CH_3), 1.41 (2 H, sextet, CH_2CH_3), 1.69 (2 H, pentet, $COCH_2CH_2$), 2.60 (2 H, t, $COCH_2$), 3.02 (2 H, t, $ArCH_2$), 4.33 (2 H, t, CH_2–O), 7.06 (1 H, t, C-6-H), 7.14 (1 H, d, C-5-H), 7.18 (1 H, t C-7-H) and 7.94 (1 H, d, C-8-H); δ_C(75 MHz; $CDCl_3$) 13.84 (q, CH_3), 22.43 (t, CH_2CH_3), 26.52 (t, $ArCH_2$), 26.62 (t, $COCH_2CH_2$), 33.54 (t, $COCH_2$), 70.54 (t, CH_2–O), 120.93 (d, C-8), 122.96 (s, C-4a), 124.44 (d, C-6), 126.18 (d, C-7), 128.74 (d, C-5), 136.57 (s, C-8a) and 172.12 (s, CO); *m*/*z* 219 (35%, M^+), 135 (100), 57 (32) and 41 (28) (Found *M*, 219.126. $C_{13}H_{17}NO_2$ requires 219.1259).

O-(2-Phenylethyl) *N*-chloro-2-ethylbutyrohydroxamate (**2f**) afforded after work-up N-(2-*ethylbutanoyl*)-3,4-*dihydro*-1H-2,1-*benzoxazine* (**3f**) (17%) as an oil; $\nu_{max}(CHCl_3)/cm^{-1}$ 1668 (CO), 1489, 1457 and 1389; δ_H(300 MHz; $CDCl_3$) 0.95 (6 H, t, 2 CH_3), 1.57 (2 H, m, $CHCH_3$), 1.73 (2 H, m, $CHCH_3$), 2.99 (m, COCH), 3.05 (2 H, t, CH_2–Ar), 4.37 (2 H, t, CH_2–O), 7.07 (1 H, t, C-6-H), 7.15 (1 H, d, C-5-H), 7.19 (1 H, t, C-7-H) and 8.0 (1 H, d, C-8-H); δ_C(75 MHz; $CDCl_3$) 11.95 (q, 2 CH_3), 24.94 (t, CH_2CH_3), 26.62 (t, $ArCH_2$), 45.04 (d, COCH), 70.90 (t, CH_2–O), 121.08 (d, C-8), 123.29 (s, C-4a), 124.54 (d, C-6), 126.17 (d, C-7), 128.81 (d, C-5), 136.74 (s, C-8a) and 174.93 (s, CO); *m*/*z* 233 (42%, M^+), 135 (100), 71 (30) and 43 (36) (Found *M*, 233.1449. $C_{14}H_{19}NO_2$ requires 233.1416).

O-(2-Phenylethyl) *N*-chloropropanohydroxamate (**2g**) afforded, after work-up nearly pure N-*propanoyl*-3,4-*dihydro*-1H-2,1-*benzoxazine* (**3g**) (71%) which crystallised from benzene–hexane as prisms, mp 60–62 °C (Found: C, 68.8; H, 7.0; N, 6.9. $C_{11}H_{13}NO_2$ requires C, 69.1; H, 6.9; N 7.3%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1674 (CO), 1489, 1457, 1379, 1292 and 1282; δ_H(300 MHz; $CDCl_3$) 1.20 (3 H, t, CH_3), 2.63 (2 H, q, CH_2CH_3), 3.04 (2 H, t, $ArCH_2$), 4.35 (2 H, t, CH_2–O), 7.07 (1 H, t, C-6-H), 7.15 (1 H, d, C-5-H), 7.19 (1 H, t, C-7-H) and 7.95 (1 H, d, C-8-H); δ_C(75 MHz; $CDCl_3$) 8.43 (q, CH_3), 26.47 (t, $ArCH_2$), 27.00 (t, CH_2CH_3), 70.33 (t, CH_2–O), 120.67 (d, C-8), 122.83 (s, C-4a), 124.28 (d, C-6), 126.03 (d, C-7), 128.65 (d, C-5), 136.44 (s, C-8a) and 172.55 (s, CO); *m*/*z* 191 (23%, M^+), 136 (22), 135 (100), 120 (17), 106 (18), 78 (16) and 57 (53).

O-(2-Phenylethyl) *N*-chloro-2-methylbutyrohydroxamate (**2h**) afforded, after work-up and centrifugal chromatography, N-2-*methylbutanoyl*-3,4-*dihydro*-1H-2,1-*benzoxazine* (**3h**) which was a pale yellow oil (78%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1663 (CO), 1489, 1457, 1386, 1310, 1295, 1280, 1243, 1074, 1060 and 1017; δ_H(300 MHz; $CDCl_3$) 0.95 (3 H, t, CH_2CH_3), 1.19 (3 H, d, $CHCH_3$), 1.50 and 1.80 (2 H, 2 × m, CH_2CH_3), 2.97 (2 H, t, $ArCH_2$), 3.05 (1 H, m, CH), 4.31 (2 H, t, CH_2–O), 7.03 (1 H, t, C-6-H), 7.11 (1 H, d, C-5-H), 7.16 (1 H, t, C-7-H) and 7.97 (1 H, d, C-8-H); δ_C(75 MHz; $CDCl_3$) 11.64 (q, CH_2CH_3), 16.61 (q, $CHCH_3$), 26.34 and 26.44 (2 × t, CH_2CH_3 and $ArCH_2$), 37.90 (d, COCH), 70.72 (t, CH_2–O), 120.80 (d, C-8), 123.04 (s, C-4a), 124.27 (d, C-6), 125.91 (d, C-7), 128.63 (d, C-5), 136.58 (s, C-8a) and 175.22 (s, CO); *m*/*z* 219 (15%, M^+), 135 (100), 57 (70) and 41 (14) (Found *M*, 219.1256. $C_{13}H_{17}NO_2$ requires 219.1259).

Thermal decomposition of *N*-acyl-3,4-dihydro-1*H*-2,1-benzoxazines

***N*-Benzoyl-3,4-dihydro-1*H*-2,1-benzoxazine (3a) in a melt.** *N*-Benzoyl-3,4-dihydro-1*H*-2,1-benzoxazine (0.31 g, 1.3 mmol) was melted in an oil bath in a sealed system under a stream of nitrogen. The nitrogen gas was bubbled through a methanolic solution of 2,4-dinitrophenylhydrazine. Melting between 149–151 °C was accompanied by a vigorous evolution of formaldehyde after which the reaction was maintained several degrees above the melting point until all evolution of gas ceased. Upon cooling to room temperature, the mixture solidified as 2-*phenyl*-4H-3,1-*benzoxazine* (**5a**) which recrystallised from methanol as colourless feathers, mp 88–90 °C (lit.,[11] 90.8–92.0 °C) (Found: C, 79.95; H, 5.3; N, 6.5. $C_{14}H_{11}NO$ requires C, 80.4; H, 5.3; N 6.7%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1624 (C=N), 1600, 1575 and 1485 (all strong) (lit.,[11] 1623, 1605, 1577); λ_{max}(ethanol)/nm 202.8 (ε/dm^3 mol^{-1} cm^{-1} 24 231), 232 (17 678) and 304 (14 537) [lit.,[11] 307 (13 183)]; δ_H(300 MHz) and δ_C(75 MHz) data are presented in Tables 1 and 2; *m*/*z* 209 (100%, M^+), 208 (28), 105 (74), 77 (66) and 51 (27). Filtration of the methanolic solution afforded orange crystals of the 2,4-dinitrophenylhydrazone of formaldehyde which were identical (IR, NMR, mp) to an authentic specimen. The product of a repeat reaction, after cooling was dissolved in 5 ml acetonitrile and analysed by HPLC using authentic 2-phenyl-4*H*-3,1-benzoxazine (**5a**) as standard. Overall conversion was 93%.

2-Phenyl-4*H*-3,1-benzoxazine (**5a**) with a cold ethanolic solution of picric acid afforded dark brown crystals of the picrate, mp 168–171 °C (lit.,[11] 170 °C).

2-Phenyl-4*H*-3,1-benzoxazine (**5a**) (0.1 g) was dissolved in cold 10% aqueous hydrochloric acid. Addition of dilute sodium hydroxide regenerated an oil which was extracted into $CDCl_3$ and dried. The ^{1}H NMR ($CDCl_3$) spectrum was identical to that of authentic 2-phenyl-4*H*-3,1-benzoxazine (**5a**).

***N*-Benzoyl-3,4-dihydro-1*H*-2,1-benzoxazine (3a) in mesitylene.** *N*-Benzoyl-3,4-dihydro-1*H*-2,1-benzoxazine (**3a**) (0.25 g, 1.04 mmol) in mesitylene (10 cm^3) was refluxed for 2.5 h. TLC and HPLC performed over the course of the reaction indicated gradual interconversion of 2,1-benzoxazine to the 3,1-benzoxazine. Removal of mesitylene *in vacuo* afforded white feathers which were identical (NMR, HPLC and mp) to the authentic material.

***N*-Acetyl-3,4-dihydro-1*H*-2,1-benzoxazine (3b) in a melt.** *N*-Acetyl-3,4-dihydro-1*H*-2,1-benzoxazine (**3b**) (0.3 g, 1.7 mmol) was melted and decomposed between 170 and 175 °C to afford an oil. NMR analysis of the melt indicated the presence of mainly 2-*methyl*-4H-3,1-*benzoxazine* (**5b**); $\nu_{max}(CHCl_3)/cm^{-1}$ 1636 (C=N), 1606, 1587, 1486, 1461, 1387 and 1249; δ_H(300 MHz) and δ_C(75 MHz) data presented in Tables 1 and 2; *m*/*z* 148 (35%, $M^+ + 1$), 147 (32, M^+), 146 (95, $M^+ - 1$), 135 (30), 119 (43), 106 (55), 105 (100), 104 (25) and 43 (50) (Found *M*, 147.0684. C_9H_9NO requires 147.0684). Attempted separation by centrifugal chromatography resulted in the isolation of only one major component as an oil, the IR, NMR and mass

spectra of which were consistent with *o*-aminobenzyl acetate (**9**. R = CH_3) (0.14 g, 0.9 mmol); $\nu_{max}(CHCl_3)/cm^{-1}$ 3478, 3396 (NH_2), 1745 (CO), 1634 (ArC=C), 1507, 1392 and 1264; δ_H(300 MHz; $CDCl_3$) 2.08 (3 H, s, CH_3), 4.05 (2 H, br, NH_2), 5.08 (2 H. s, CH_2), 6.70 (1 H, d, *m*-H), 6.75 (1 H, t, *m'*-H), 7.15 (1 H, t, *p*-H), 7.19 (1 H, d, *o'*-H); δ_C(75 MHz; $CDCl_3$) 20.97 (q, CH_3), 64.18 (t, CH_2), 116.12 (d, *m*-C), 118.37 (d, *m'*-C), 120.15 (s, C^i), 130.09 and 131.42 (ds, *p*-C and *o'*-C), 145.88 (s, *o*-C) and 171.27 (s, CO); *m/z* 165 (72%, M^+), 147 (36), 106 (85), 105 (100), 103 (65), 78 (35), 60 (54), 45 (50) and 43 (63) (Found *M*, 165.0764. $C_9H_{11}NO_2$ requires 165.0789).

Neat *o*-aminobenzyl acetate (**9**, R = CH_3), upon standing, rearranged to *o*-hydroxymethyl acetanilide (**10**, R = CH_3), which recrystallised from benzene–hexane as needles, mp 115 °C (lit.,[25] 115–116 °C); $\nu_{max}(CHCl_3)/cm^{-1}$ 3594 (OH), 3383 (NH), 3010, 1683 (CO), 1590, 1526 and 1453; δ_H(300 MHz; $CDCl_3$) 1.6 (1 H, br, OH), 2.19 (3 H, s, CH_3), 4.70 (2 H, s, CH_2), 7.09 (1 H, t, *p*-H), 7.19 (1 H, d, *m*-H), 7.34 (1 H, t, *m'*-H), 8.01 (1 H, d, *o'*-H) and 8.51 (1 H, br, NH); δ_C(75 MHz; $CDCl_3$) 24.50 (q, CH_3), 64.12 (t, CH_2), 122.69 (d, *o'*-C), 124.44 (d, *p*-C), 128.84 and 128.94 (2 × d, *m*- and *m'*-Cs), 130.01 (s, *o*-C), 137.23 (*s*, C^i) and 169.13 (s, CO).

Hydrolysis of 2-methyl-4*H*-3,1-benzoxazine (5b). 2-Methyl-4-*H*-3,1-benzoxazine (**5b**) (0.2 g, 1.4 mmol), in a 4:1 mixture of acetonitrile and water (2 cm^3), was monitored by ^1H NMR spectroscopy. Over a period of 3.6 h, **5b** (singlet at δ 5.21) was completely replaced by **9** (R = CH_3) (singlet at δ 5.08) and an unknown (singlet at δ 5.01) which in turn converted to **9** (R = CH_3) over several days. **9** (R = CH_3) decomposed slowly to a mixture which contained **10** (R = CH_3).

***N*-Pivaloyl-3,4-dihydro-1*H*-2,1-benzoxazine (3c) in a melt.** *N*-Pivaloyl-3,4-dihydro-1*H*-2,1-benzoxazine (**3c**) (0.3 g, 1.4 mmol) was melted and heated until evolution of formaldehyde ceased. The resultant oil was nearly pure 2-tert-*butyl*-4H-3,1-*benzoxazine* (**5c**); $\nu_{max}(CHCl_3)/cm^{-1}$ 1641 (C=N), 1616, 1596, 1496, 1471 and 1147 (all strong); δ_H(300 MHz) and δ_C(75 MHz) data presented in Tables 1 and 2; *m/z* 207 (23, $M^+ + H_2O$), 189 (25, M^+), 188 (95, $M^+ - 1$), 132 (65, $M^+ - Bu^t$), 119 (75, M^+ – dimethylketene), 106 (25), 105 (40), 104 (25) and 57 (100).

***N*-Pivaloyl-3,4-dihydro-1*H*-2,1-benzoxazine (3c) in mesitylene.** *N*-Pivaloyl-3,4-dihydro-1*H*-2,1-benzoxazine (**3c**) (0.25 g, 1.1 mmol) was refluxed in mesitylene (10 cm^3). HPLC analysis after 40 min indicated complete conversion to 2-*tert*-butyl-4*H*-3,1-benzoxazine (**5c**) which was isolated by removal of mesitylene under reduced pressure and was a light yellow oil.

***N*-2-Methylpropanoyl-3,4-dihydro-1*H*-2,1-benzoxazine (3d) in a melt.** *N*-2-Methylpropanoyl-3,4-dihydro-1*H*-2,1-benzoxazine (**3d**) (0.3 g, 1.5 mmol) was melted and heated until evolution of formaldehyde ceased. The resultant oil contained unreacted 2,1-benzoxazine (12% by ^1H NMR spectroscopy) and a second, major component (88%) which was isolated by centrifugal chromatography as an oil of 2-*isopropyl*-4H-3,1-*benzoxazine* (**5d**); $\nu_{max}(CHCl_3)/cm^{-1}$ 1629 (C=N), 1604, 1587, 1487, 1459, 1388 and 1145; λ_{max}(ethanol)/nm 212 (ε/dm^3 mol^{-1} cm^{-1} 14 640) and 246 (5956); δ_H(300 MHz) and δ_C(75 MHz) data are presented in Tables 1 and 2; *m/z* 193 (8, $M^+ + H_2O$), 175 (75, M^+), 160 (60, $M^+ - CH_3$), 132 (100, M^+ – isopropyl), 106 (26), 105 (30), 104 (24) and 43 (45) (Found *M*, 175.0959. $C_{11}H_{13}NO$ requires 175.0997).

***N*-2-Methylpropanoyl-3,4-dihydro-1*H*-2,1-benzoxazine (3d) in mesitylene.** *N*-2-Methylpropanoyl-3,4-dihydro-1*H*-2,1-benzoxazine (**3c**) (0.25 g, 1.2 mmol) was refluxed in mesitylene (10 cm^3) until HPLC analysis revealed complete conversion to 2-isopropyl-4*H*-3,1-benzoxazine (**5d**) which was isolated by removal of mesitylene under reduced pressure and was an oil.

***N*-Pentanoyl-3,4-dihydro-1*H*-2,1-benzoxazine (3e) in a melt.** *N*-Pentanoyl-3,4-dihydro-1*H*-2,1-benzoxazine (**3e**) (0.1 g, 0.5 mmol) was melted and heated until evolution of formaldehyde ceased. The resultant oil was nearly pure 2-*butyl*-4H-3,1-*benzoxazine* (**5e**); $\nu_{max}(CHCl_3)/cm^{-1}$ 1630 (C=N), 1605, 1588, 1486, 1460 and 1381; δ_H(300 MHz) and δ_C(75 MHz) data presented in Tables 1 and 2; *m/z* CI (CH_4) 190 ($M^+ + 1$); *m/z* EI 207 (36, $M^+ + H_2O$), 189 (7, M^+), 188 (6, $M^+ - 1$), 174 (20, $M^+ - 14$), 161 (42, $M^+ - 28$), 147 (38, $M^+ - 42$), 106 (40), 105 (100), 104 (20), 91 (15), 77 (14), 57 (25) and 41 (25) (Found *M*, 189.1147. $C_{12}H_{15}NO$ requires 189.1154). The crude material decomposed during centrifugal chromatography.

***N*-(2-Ethylbutanoyl)-3,4-dihydro-1*H*-2,1-benzoxazine (3f) in a melt.** *N*-(2-Ethylbutanoyl)-3,4-dihydro-1*H*-2,1-benzoxazine (**3f**) (0.1 g, 0.5 mmol) was melted and heated until evolution of formaldehyde ceased. The resultant oil was nearly pure 2-(3-*pentyl*)-4H-3,1-*benzoxazine* (**5f**); $\nu_{max}(CHCl_3)/cm^{-1}$ 1627 (C=N), 1604, 1586, 1486, 1460 and 1380; δ_H(300 MHz) and δ_C(75 MHz) data are presented in Tables 1 and 2; *m/z* 219 (8, $M^+ + H_2O$), 203 (42, M^+), 202 (17, $M^+ - 1$), 188 (55, $M^+ - 15$), 175 (83, $M^+ - 28$, McLafferty), 174 (85, M^+ – Et), 160 (92, $M^+ - C_3H_7$), 146 (63, $M^+ - C_4H_9$), 132 (78, $M^+ - C_5H_{11}$), 106 (76), 105 (55), 104 (50), 91 (23), 77 (50), 71 (52, C_5H_{11}), 55 (40) and 43 (100, C_3H_7) (Found *M*, 203.1286. $C_{13}H_{17}NO$ requires 203.1310). Separation was not attempted.

***N*-Propanoyl-3,4-dihydro-1*H*-2,1-benzoxazine (3g) in a melt.** *N*-Propanoyl-3,4-dihydro-1*H*-2,1-benzoxazine (**3g**) (0.1 g, 0.5 mmol) was melted and heated until evolution of formaldehyde ceased. The resultant pale red oil was nearly pure 2-*ethyl*-4H-3,1-*benzoxazine* (**5c**); $\nu_{max}(CHCl_3)/cm^{-1}$ 1641 (C=N), 1616, 1596, 1496, 1471, 1391, 1197 and 1177; δ_H(300 MHz) and δ_C(75 MHz) data are presented in Tables 1 and 2; *m/z* 179 (7, $M^+ + H_2O$), 161 (85, M^+), 160 (95, $M^+ - 1$), 132 (100, M^+ – Et), 106 (27), 105 (10), 104 (22), 78 (20) and 77 (25) (Found *M*, 161.0835. $C_{10}H_{11}NO$ requires 161.0841). The crude material decomposed during centrifugal chromatography.

***N*-2-Methylbutanoyl-3,4-dihydro-1*H*-2,1-benzoxazine (3h) in a melt.** *N*-2-Methylbutanoyl-3,4-dihydro-1*H*-2,1-benzoxazine (**3h**) (0.1 g, 0.5 mmol) was melted and heated until evolution of formaldehyde ceased. The resultant oil was nearly pure 2-(2-*butyl*)-4H-3,1-*benzoxazine* (**5h**); $\nu_{max}(CHCl_3)/cm^{-1}$ 1628 (C=N), 1604, 1586, 1486, 1459 and 1383; δ_H(300 MHz) and δ_C(75 MHz) data are presented in Tables 1 and 2; *m/z* 207 (8, $M^+ + H_2O$), 189 (38, M^+), 174 (50, $M^+ - 15$), 161 (100, $M^+ - 28$, McLafferty), 132 (100, $M^+ - C_4H_9$), 106 (47), 105 (43), 104 (30), 91 (22), 85 (20) and 57 (62) (Found 189.1160. $C_{12}H_{15}NO$ requires 189.1154). Separation was not attempted.

Irradiation of 2-phenyl-4*H*-3,1-benzoxazine in methanol

2-Phenyl-4*H*-3,1-benzoxazine (8.2 mg, 0.04 mmol) in methanol (3 cm^3) was stirred in the dark for 2 h. HPLC analysis revealed no reaction. Irradiation with ultraviolet light (300 nm through pyrex) effected rapid consumption of the oxazine. Removal of solvent under vacuum followed by centrifugal chromatography afforded an oil which was 2-*methoxymethylbenzanilide* (**11a**); $\nu_{max}(CHCl_3)/cm^{-1}$ 3360 (bonded NH only), 1680 (CO), 1603 (Ar), 1541, 1465, 1336 and 1090; δ_H(300 MHz; $CDCl_3$) 3.44 (3 H, s, CH_3), 4.63 (2 H, s, CH_2), 7.09 (1 H, t, C-4-H), 7.20 (1 H, d, C-3-H), 7.41 (1 H, t, C-5-H), 7.3–7.6 (3 H, m, C-3'-, C-4'-, C-5'-H), 7.92 (2 H, d, C-2'-, C-6'-H), 8.41 (1 H, d, C-6-H) and 9.6 (1 H, br s, NH); δ_C(75 MHz; $CDCl_3$) 57.80 (q, CH_3), 74.26 (t, CH_2), 121.65 (d, C-6), 123.79 (d, C-4), 125.99 (s, C-2), 127.01 (d, C-2' and C-6'), 128.81 (d, C-3' and C-5'), 129.36 and 129.42 (2 × d, C-3 and C-5), 131.81 (d, C-4'), 134.83 (s, C-1'), 138.15 (s, C-1) and 165.04 (s, CO); *m/z* 241 (25%, M^+), 226 (26, $M^+ - CH_3$), 209 (36, $M^+ - CH_3O$), 105 (100) and 77 (50) (Found 241.1031. $C_{15}H_{15}NO_2$ requires 241.1102). HPLC analysis of a repeat experiment indicated the formation of **11a** in 88% yield.

2-Phenyl-4*H*-3,1-benzoxazine (8.8 mg, 0.04 mmol) in dry, distilled cyclohexanol (2 cm^3) was stirred at 160 °C in the dark for 1.6 h. HPLC analysis revealed no reaction. Irradiation at room temperature with UV light (300 nm through pyrex)

Table 4 Rate constants for decomposition of *N*-benzoyl- (**3a**), *N*-pivaloyl- (**3c**) and *N*-(2-methylpropanoyl)-3,4-dihydro-1*H*-2,1-benzoxazine (**3d**) in mesitylene

3a		**3c**		**3d**	
T/°C	$k/10^{-4}$ s^{-1}	T/°C	$k/10^{-4}$ s^{-1}	T/°C	$k/10^{-4}$ s^{-1}
158.0	2.883	156.5	9.709	158.0	0.911
149.0	1.230	148.5	4.755	148.0	0.296
139.8	0.484	140.0	1.878	139.5	0.102
130.2	0.140	129.5	0.640		

effected consumption of the oxazine. Removal of cyclohexanol under reduced pressure followed by centrifugal chromatography afforded an oil which was *2-cyclohexyloxymethylbenzanilide* (**11b**); $\nu_{max}(CHCl_3)$/cm^{-1} 3360 (bonded NH only), 1680 (CO), 1605 (Ar), 1595, 1541, 1465, 1315 and 1080; δ_H(300 MHz; $CDCl_3$) 1.10–2.42 (5 H, m), 1.5–1.6 (1 H, m), 1.65–1.82 (2 H, m), 1.9–2.05 (2 H, m), 3.40 (1 H, m, OCH), 4.66 (2 H, s, CH_2), 7.05 (1 H, t, C-4-H), 7.16 (1 H, d, C-3-H), 7.36 (1 H, t, C-5-H), 7.4–7.6 (3 H, m, C-3′-, C-4′-, C-5′-H), 7.95 (2 H, d, C-2′-, C-6′-H), 8.41 (1 H, d, C-6-H) and 9.8 (1 H, br s, NH); δ_C(75 MHz; $CDCl_3$) 23.78 (t, C-3″ and C-5″), 25.51 (t, C-4″), 31.96 (t, C-2″ and C-6″), 69.20 (t, OCH_2), 76.73 (d, OCH), 121.47 (d, C-6), 123.58 (d, C-4), 126.92 (s, C-2), 127.00 (d, C-2′ and C-6′), 128.51 (d, C-3′ and C-5′), 128.88 (2 × d, C-3 and C-5), 131.61 (d, C-4′), 134.96 (s, C-1′), 138.22 (s, C-1) and 165.07 (s, CO); *m/z* 309 (65%, M^+), 226 (17, M^+ − cyclohexyl), 105 (100) and 77 (32) (Found 309.1698. $C_{20}H_{23}NO_2$ requires 309.1728). HPLC analysis of a repeat experiment indicated the formation of **11b** in 66% yield.

Thermolysis of *N*-benzoyl-3,4-dihydro-1*H*-2,1-benzoxazine in cyclohexanol

N-Benzoyl-3,4-dihydro-1*H*-2,1-benzoxazine (**3a**) (28.2 mg, 0.13 mmol) was refluxed in dry, distilled cyclohexanol (5 cm^3) until HPLC indicated complete conversion of the reactant. HPLC analysis using authentic materials as standards indicated the formation of 2-phenyl-4*H*-3,1-benzoxazine (**5a**) (82.4%) and 2-cyclohexyloxymethylbenzanilide (**11b**) (12.5%).

Synthesis of benzyl acetimidate (8)[12,26]

Benzyl alcohol (26.3 g, 0.24 mol) and anhydrous acetonitrile (10 g, 0.24 mol) were cooled to 0 °C followed by addition of dry hydrogen chloride (8.9 g, 0.52 mol) through a bubbler. The mixture was refrigerated until all liquid was replaced by a solid cake of benzyl acetimidate hydrochloride. A portion of the salt was stirred in anhydrous ether in the presence of excess anhydrous Na_2SO_4 and $NaHCO_3$ (1:1) until evolution of CO_2 ceased. Filtration and concentration of the ether afforded pure benzyl acetimidate as a colourless oil, $\nu_{max}(CHCl_3)$/cm^{-1} 3337 (NH), 1658 (CO), 1396, 1326 and 1092; δ_H(300 MHz; $CDCl_3$) 1.98 (3 H, s, CH_3), 5.08 (2 H, s, CH_2), 7.15–7.4 (5 H, m, ArH) and 7.0 (1 H, br s, NH); δ_C(75 MHz; $CDCl_3$) 21.96 (q, CH_3), 66.92 (t, CH_2), 127.35, 127.95 and 128.2 (3 × d, *o*-, *m*- and *p*-C), 136.45 (s, C^i) and 168.97 (s, CO).

Rate studies

Rates of decomposition of *N*-benzoyl-, *N*-pivaloyl and *N*-(2-methylpropanoyl)-3,4-dihydro-1*H*-2,1-benzoxazines were determined in mesitylene using diphenyl as internal standard and aliquots were analysed by reverse phase HPLC (Table 4). Reaction mixtures were thermostatted at temperatures between 125 and 160 °C and followed first-order kinetics.

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