Superbase catalysis of oxazolidin-2-one ring formation from carbon dioxide and prop-2-yn-1-amines under homogeneous or heterogenous conditions

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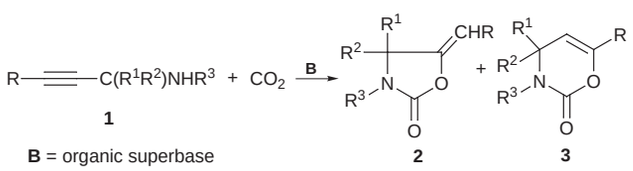
***N*-alkyl-substituted prop-2-yn-1-amines and *N*-tri-, tetra- and penta-alkyl-substituted guanidines or other strong organic bases assemble under the action of carbon dioxide to afford carbamates, from which methyleneoxazolidinones 2 are formed by ring closure. If alkyl or cycloalkyl chains of appropriate length are present in the guanidines the reaction readily occurs under heterogenous conditions without solvent.**

Introduction

We have recently shown that the catalytic use of superbases allows the direct introduction of carbon dioxide into acetylenic amines[1] under mild conditions in acetonitrile to give fair to excellent yields of **2**, corresponding to 5-*exo*-*dig* ring closure in agreement with Baldwin's rules.[2] A few percent of **3** (6-*endo*-*dig* cyclization) is formed only in stoichiometric reactions at temperatures higher than 100 °C, see Scheme 1.



1a R = H; R^1 = R^2 = H; R^3 = Me
b R = H; R^1 = R^2 = H; R^3 = Bu^n
c R = H; R^1 = R^2 = H; R^3 = CH_2Ph
d R = H; R^1 = H; R^2 = Me; R^3 = Bu^n
e R = H; R^1 = R^2 = Me; R^3 = Bu^n
f R = H; R^1 = R^2 = Me; R^3 = CH_2Ph
g R = H; R^1 = R^2 = Me; R^3 = *n*-C_6H_{13}
h R = H; R^1 = R^2 = Me; R^3 = $CH_2CH{=}CH_2$
i R = Me; R^1 = R^2 = H; R^3 = CH_2Ph

Scheme 1

The use of strong bases able to stabilize the intermediate carbamate anion was the key for the success of this reaction. We now report additional results and new developments including the generation of hydrophobic regions between the substrate and superbase, which allow the reaction to be carried out in the presence of water much alike enzyme catalysis. Further information about the intermediates involved and the role of hydrogen bridges are also provided.

Results and discussion

Reactions in homogeneous solution

With carbon dioxide. The reactions can be performed in organic solvents able to dissolve the carbamates formed from the secondary acetylenic amine, carbon dioxide and the strong base (Scheme 2).

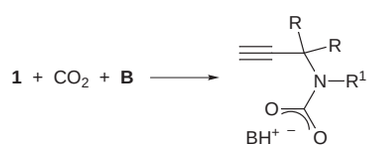
The model we chose was based on the interaction of an acid with a guanidine compound, which has been recently reported,[3] and that we assumed to be also valid for the carbamic acid case.

As previously observed[1] some strong bases especially those having $pK_{BH^+} \geqslant 24$ in acetonitrile gave satisfactory yields under very mild reaction conditions. Table 1 summarizes yields and conversions of catalytic reactions using superbases of different nature and strength.

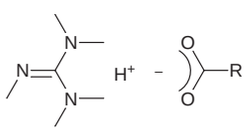
Table 1 Catalytic reaction of amine $HC{\equiv}CC(Me)_2NHCH_2Ph$ **1f** with CO_2 in the presence of strong bases in acetonitrile[a]

Entry	Base ($^{MeCN}pK_{BH^+}$)[6]	Conversion (%)[b]	**2f** Yield (%)[c]
1	**5b** (25.44)	>99	89
2	**4b** (24.2)	95	83
3	**5a** (25.95)	89	78
4	**4a** (23.75)	75	64
5	**6** (24.33)	80	75
6	**10** (42.60)	90	83
7	**11** (27.58)	55	50
8	**8**[d]	68	60
9	**4k**[d]	>99	89
10	**9**[d]	98	87
11	**4l**[d]	81	76
12	**4f**[d]	>99	89
13	**4c**[d]	79	74
14	**4d**[d]	48	42
15	**4e**[d]	95	88
16	**4g**[d]	99	88
17	**4h**[d]	>99	89

[a] Reaction conditions: 80 °C, 6 bar CO_2, 6 h; amine **1f** (2 mmol, amine : base molar ratio 10 : 1, base conc. 0.125 mol dm^{-3}). [b] With respect to the starting acetylenic amine. [c] Yield of isolated products with respect to the starting acetylenic amine. [d] pK_{BH^+} values are not available but should be placed between 24.5 and 23.5.



Scheme 2

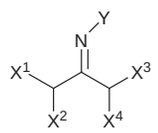


To our knowledge, pK_{BH^+} measurements of guanidines **4c**–**h**,**k**,**l**, **8** and **9** have not been reported. However, on the basis of previous studies pK_{BH^+} values can be confidently assumed to be not very different from those of the corresponding methyl-substituted guanidines for which pK_{BH^+} values near 13.4–13.9 have been obtained in water.[4] Slightly lower values than those found for methylated guanidines should be expected however: methyl group homologues cause a slight decrease in basicity according to the trend observed with primary amines.[5a] The differences in the pK_{BH^+} values of various guanidines in

Table 2 Stoichiometric reaction of amine $HC{\equiv}CC(Me)_2NHCH_2Ph$ **1f** with CO_2 in the presence of strong bases in acetonitrile[a]

Entry	Base ($^{MeCN}pK_{BH^+}$)[6]	Conversion (%)[b]	**2f** Yield (%)[b]	**3f** Yield (%)[b]
1	**5b** (25.44)	>99	93	3
2	**4b** (24.2)	>99	92	3
3	**5a** (25.95)	>99	92	2.5
4	**4a** (23.75)	>99	83	2
5	**6** (24.33)	90	75	2
6	**10** (42.60)	91	78	—
7	**11** (27.58)	59	46	—
8	**4i** (17.90)	30	18	8
9	**7** (18.50)	10	4	—

[a] Reaction conditions: 110 °C, 10 bar CO_2, 24 h, amine **1f** (1 mmol, base conc. 0.2 mol dm^{-3}). [b] By GLC based on the starting acetylenic amine.



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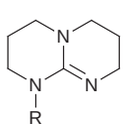
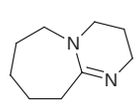
4a $X^1 = X^2 = X^3 = X^4 = Me$, Y = H
4b $X^1 = X^2 = X^1 = X^4 = Me$, Y = Pr
4c $X^1 = X^2 = X^3 = X^4 = Me$, Y = octyl
4d $X^1 = X^2 = X^3 = X^4 = Me$, Y = dodecyl
4e $X^1 = X^2 = X^3 = X^4 = Me$, Y = cyclohexyl
4f $X^1 = X^3 = H$, $X^2 = X^4 = Pr^i$, Y = dodecyl
4g $X^1 = X^3 = H$, $X^2 = X^4 = Pr^i$, Y = cyclohexyl
4h $X^1 = X^3 = H$, $X^2 = X^4 = Y = Pr^i$
4i $X^1 = X^3 = Y = H$, $X^2 = X^4 = Ph$
4k $X^1 = X^3 = H$, $X^2 = X^4 = Y =$ cyclohexyl
4l $X^1 = X^3 = H$, $X^2 = X^4 =$ cyclohexyl, Y = dodecyl



5a R = H
5b R = Me

5



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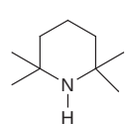

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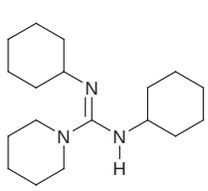

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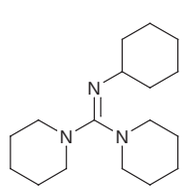

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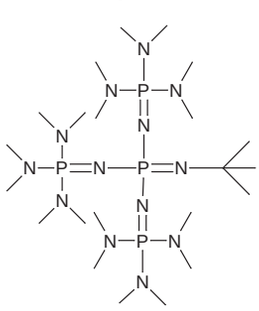

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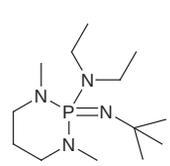

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acetonitrile should also be small as found in water, although distributed over a larger range.[5b] Taking into account that 1,1,3,3-tetramethylguanidine has a $pK_{BH^+} = 23.75$ in acetonitrile, pentamethylguanidine = 25 and propyltetramethylguanidine = 24.2, values between 23.5 and 24.5 should cover all the range of substituted guanidines used in the present work.[6] This seems sufficient for the present study because as we shall see, basicity is not the only factor influencing the reaction described here; other conditions need to be considered to obtain satisfactory results. Thus, some ring-containing pentaalkyl-substituted guanidines work better than the tetraalkyl ones (compare entries 1, 2, 10 and 15 with 3, 4 and 8) even in the case when the latter have higher pK_{BH^+} values (compare entries 1 and 3). However, elongating one aliphatic chain in pentalkylguanidines gives less satisfactory results (entries 13 and 14). Good results are obtained with trialkylguanidines (entries 9, 12, 16, 17 and, to a lesser extent, 11). The effect of basicity is apparent with the phosphorus bases **10** and **11** (entries 6 and 7) where **10** (pK_{BH^+} 42.60) gives a higher yield than **11** (pK_{BH^+} 27.58). The amidine **6** (entry 5) also behaves satisfactorily. In conclusion the course of the reaction turns out to be influenced not only by basicity but also by other structural effects probably ascribable to steric hindrance and to hydrogen bridges as will be discussed later.

Table 3 Reaction of different amines $[RC{\equiv}CC(R^1R^2)NHR^3]$ **1** with CO_2 and **4a**[a]

Entry	Starting material	Conversion (%)[b]	Product **2**	Yield (%)[c]
1	**1a**	69	**2a**	58[d]
2	**1d**	75	**2d**	70[d]
3	**1e**	90	**2e**	83
4	**1f**	91	**2f**	79
5	**1h**	70	**2h**	60
6	**1i**	25	**2i**	18[e]

[a] Reaction conditions: 110 °C, 5 bar CO_2, 24 h, acetylenic amine (2 mmol, amine : base molar ratio 10 : 1, base conc. 0.045 mol dm^{-3}). [b] With respect to the starting acetylenic amine. [c] Isolated products with respect to the starting acetylenic amines. [d] Base conc. 0.2 mol dm^{-3}. [e] At 140 °C for 48 h, base conc. 0.2 mol dm^{-3}.

Under more drastic conditions and with stoichiometric ratios of the base, high yields of **2** were usually attained together with small amounts of the six-membered ring **3** as shown in Table 2. Guanidines with high pK_{BH^+} values did not differ very strongly from each other in activity (entries 1–4), however. Lower yields were obtained with **4i** and **7** (entries 8, 9) likely owing to their lower basicity, and with **11**, likely as a consequence of its steric bulk (entry 7).

The dependence of the yield of **2** on the superbase concentration has also been studied using bases **5a** and **10** with amine **1f** (10 : 1 molar ratio) at 80 °C under 6 bar of CO_2 for 6 h. The results indicate that the yield of **2f** increases from 27 to 89% on increasing the concentration of superbase **5a** from 0.02 to 0.12 mol dm^{-3} and from 20 to 83% on increasing the concentration of superbase **10** from 0.03 to 0.12 mol dm^{-3}.

The reaction was unsuccessful in weakly polar solvents such as toluene and THF. The use of aprotic polar solvents such as *N*,*N*-dimethylacetamide, *N*-methylpyrrolidone and above all acetonitrile gave the best results.

Alkyl substituents in the propynyl group of the starting material also exert an important effect on the course of the reaction. The results of catalytic reactions carried out at 110 °C for 24 h under 5 bar CO_2 pressure in acetonitrile in the presence of **4a** (1 : 10 molar ratio with the amine) are reported in Table 3.

The best yields were attained with geminal methyl groups (1,1-disubstituted) in the starting material (entries 3,4). Substituents at the terminal position of the triple bond strongly decrease the yield (entry 6).

With sodium hydrogen carbonate and NBu_4Br. The reaction described above can also be carried out using sodium hydrogen carbonate as CO_2 carrier. The best results were obtained, however, by adding NBu_4Br as phase transfer agent for the hydrogen carbonate anion from the solid to the liquid phase (Table 4).

Reactions in water

With carbon dioxide. Since the reaction involves the formation of a carbamate anion, which carries out the attack on the triple bond, it is strongly inhibited by the presence of water and

Table 4 Catalytic reaction of amine $HC{\equiv}CC(Me)_2NHCH_2Ph$ **1f** with $NaHCO_3$ in the presence of strong bases and NBu_4Br in acetonitrile[a]

Entry	Base	$NaHCO_3$: **1f** molar ratio	Conversion (%)[b]	**2f** Yield (%)[b]
1	**9**	6	64	63
2	**9**	6 + NBu_4Br	97	95
3	**8**	6	52	50
4	**8**	6 + NBu_4Br	92	90
5	**41**	6	55	54
6	**41**	6 + NBu_4Br	>99	98

[a] Reaction conditions: 80 °C, 15 h, amine (2 mmol, amine : base molar ratio 10 : 1, base conc. 0.067 mol dm^{-3}, NBu_4Br : base molar ratio 2 : 1, CH_3CN 1.5 ml). [b] By GLC based on the starting acetylenic amine.

hydrogen donors in general. On the other hand reactions of this kind are commonly effected by enzyme systems in the presence of water.[7] This is attributed to the formation of segregated sites, formed by taking advantage of both hydrophobic regions and a hydrogen bond network,[8,9] where water is prevented from interfering adversely with the reaction center.We wondered whether an appropriate, though not necessarily so efficient, site could be generated for the reaction under study in the presence of water. Carbon dioxide itself could be responsible for joining together the two reactive partners to create a hydrophobic site. To this end we had to design proper substrates and bases **B** whose assembly could ensure the exclusion of water and the access of carbon dioxide.

We ascertained that by reaction with carbon dioxide, secondary propynamines and properly sized tetra- or pentaalkylguanidines form the corresponding guanidinium carbamates, which are able to segregate so effectively from water to allow intramolecular incorporation of the intermediate carbamate into an oxazolidine ring by reaction with the triple bond, even in the absence of added carbon dioxide. Thus *N*-benzyldimethylpropynamine **1f** (1.0 mmol) and guanidine **8** (1.0 mmol) were allowed to react stoichiometrically with CO_2 (1 bar) at room temperature in the presence of water (1.8 ml), then the mixture containing the carbamate was heated at 70 °C in the absence of added CO_2 to obtain a 20% yield of **2f**. Operating a one-pot reaction under carbon dioxide gave good results as shown in Table 5. Thus **1e** (2.0 mmol) reacted with carbon dioxide (20 bar) in the presence of base **8** (2.0 mmol) in water (1.5 ml) at 70 °C for 24 h under stirring in an autoclave (45 ml capacity) giving product **2e** in 91% yield (entry 8). With **1b** and **1c** the yield was even higher (95%, entry 3, and 96%, entry 5), in contrast with that observed with **4a** in acetonitrile (Table 4) where the geminal R^1 and R^2 groups were found to exert a positive effect (this result points to the importance of the shape of the hydrophobic region in the presence of water). Interestingly the reaction could be made catalytic using 2.5 mmol of **1c** and 0.1 mmol of **8** under the same conditions still maintaining a good yield (93%, entry 6). The same reaction (4 : 1 substrate to guanidine molar ratio) could be carried out at atmospheric pressure of CO_2 at 70 °C for 24 h giving **2c** in 77% yield (entry 7; for other catalytic reactions, which were not optimized, compare entries 4, 9, 13, 14, 15 and 21). As expected the reaction of alkynamines and guanidines having short alkyl chains was not satisfactory, for example *N*-methylprop-2-ynamine **1a** or *N*-benzyl-1,1-dimethylprop-2-ynamine **1f** and tetramethylguanidine (**4a**) in stoichiometric amounts in the presence of water gave <1% and 3% yield of **2a** and **2f**, respectively (entries 1 and 17). The presence of medium-sized alkyl chains such as *n*-butyl or benzyl groups at the nitrogen of propynamines is beneficial (entries 3, 5, 8, 18). Longer chains (C_{10}) have a negative effect. Thus the stoichiometric reaction of *N*-decyldimethylpropynamine with carbon dioxide and base **4c**, under the reported conditions, gave a 2% yield of **2**. On the other hand cyclic or long-chain aliphatic groups replacing hydrogen in one NH group of tetramethylguanidine such as **4c** and **4e** as well as other variants (**8**, **9**) exert a positive effect (compare entries 1, 2; 14, 15; 17, 18; 20–23). Replacing all the methyl groups with *n*-octyl chains gives negative results (less than 1% yield of **2f**). These limitations are likely to be related to the need for preserving easy access of carbon dioxide to the reaction center.

Table 5 Reaction of *N*-alkylpropynamines **1** with CO_2 in the presence of guanidine bases and water[a]

Entry	Amine **1** (mmol)	Base (mmol)	Conversion (%)[b]	**2** Yield (%)[b]
1	**1a** (2.0)	**4a** (2.0)	1	**2a** <1
2	**1a** (2.0)	**8** (2.0)	33	**2a** 31
3	**1b** (2.0)	**8** (2.0)	97	**2b** 95
4	**1b** (2.0)	**8** (0.5)	88	**2b** 87
5	**1c** (2.0)	**8** (2.0)	97	**2c** 96
6	**1c** (2.5)	**8** (0.1)	94	**2c** 93
7	**1c** (2.0)	**8** (0.5)	78	**2c** 77[c]
8	**1e** (2.0)	**8** (2.0)	93	**2e** 91
9	**1e** (2.0)	**8** (0.5)	82	**2e** 80
10	**1e** (2.0)	**8** (2.0)	87	**2e** 86[c]
11	**1e** (2.0)	**8** (2.0)	4	**2e** 3[d]
12	**1e** (2.0)	**4c** (2.0)	78	**2e** 75[c]
13	**1e** (2.0)	**4c** (0.5)	53	**2e** 51
14	**1e** (2.0)	**4e** (0.5)	50	**2e** 47
15	**1e** (2.0)	**4b** (0.5)	18	**2e** 16
16	**1g** (2.0)	**4c** (2.0)	54	**2g** 52
17	**1f** (2.0)	**4a** (2.0)	4	**2f** 3
18	**1f** (2.0)	**8** (2.0)	94	**2f** 92
19	**1f** (2.0)	**9** (2.0)	86	**2f** 80
20	**1f** (2.0)	**4c** (2.0)	79	**2f** 75
21	**1f** (2.0)	**4c** (0.5)	68	**2f** 66
22	**1f** (2.0)	**4c** (2.0)	73	**2f** 71[c]
23	**1f** (2.0)	**4f** (2.0)	>99	**2f** 94

[a] Reaction conditions: 70 °C, 20 bar CO_2, 24 h, 2.5 ml water for 2.0 mmol of amine **1**. Increasing the amount of water led to longer reaction times but did not affect yields significantly. [b] By GLC based on the starting acetylenic amine. [c] At atmospheric pressure of carbon dioxide. [d] At room temperature and atmospheric pressure of CO_2.

With sodium hydrogen carbonate and NBu_4Br. The same type of reactions as described above were tried using sodium hydrogen carbonate as CO_2 carrier. The best results were obtained as in the case of the homogeneous solution by adding NBu_4Br as phase transfer agent. Table 6 shows the results.

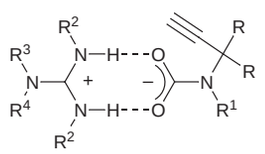
The results suggest that a complex interplay of factors control carbon dioxide incorporation, including strength of the base used, hydrogen bonding, size and shape of the catalytic assembly and hydrophobicity. While the superbase is required to stabilize the carbamate first formed, hydrogen bonds can be important to reinforce the assembly, particularly in the presence of water, a circumstance also requiring suitable substituents both in the base and in the acetylenic amine to warrant sufficient hydrophobicity while preserving facile access of carbon dioxide to the reaction center. Taking as an example the reaction of **1e** in the presence of water it can be observed that tetraalkylguanidine **8** (with one hydrogen on a nitrogen atom) works better than the pentaalkyl one **9** (compare entries 5 and 10, and 6 and 11 of Table 6). This is in contrast with what happens in acetonitrile, where the opposite was found to be true, as shown by comparative experiments, which were carried out at atmospheric CO_2 pressure to magnify the differences. Thus **1e** reacted with carbon dioxide at atmospheric pressure in the presence of pentaalkylguanidine **9** (1 mol per mol of **1e**), in acetonitrile at 70 °C for 3 h, to give oxazolidinone **2e** in 55% yield, while with tetraalkylguanidine **8**, under the same reaction conditions, the yield was 32%. Working at atmospheric pressure of carbon dioxide at 70 °C for 7 h with water in place of acetonitrile pentaalkylguanidine **9** gave an 18% yield of **2e**, while the tetraalkyl one (**8**) gave a 68% yield of **2e**. This behaviour can possibly be traced to the effect of hydrogen bonds in the intermediate guanidinium carbamate.

In the presence of water two hydrogen bonds, such as those resulting from the carbamate interaction with **8**, are more

Table 6 Catalytic reaction of acetylenic amines **1e** and **1f** with $NaHCO_3$ in the presence of strong bases and NBu_4Br in water[a]

Entry	Amine **1**	Base	$NaHCO_3$: Amine molar ratio	Conversion (%)[b]	**2** Yield (%)[b]
1	**1f**	**4d**	6	57	**2f** 56
2	**1f**	**4c**	6	38	**2f** 38
3	**1f**	**4c**	6 + NBu_4Br	85	**2f** 83
4	**1f**	**9**	6	30	**2f** 30
5	**1e**	**9**	6	33	**2e** 31
6	**1f**	**9**	6 + NBu_4Br	60	**2f** 58
7	**1f**	**8**	4	59	**2f** 58
8	**1f**	**8**	4 + NBu_4Br	88	**2f** 83
9	**1f**	**8**	6	83	**2f** 81
10	**1e**	**8**	6	64	**2e** 60
11	**1f**	**8**	6 + NBu_4Br	95	**2f** 92
12	**1f**	**4k**	6	7	**2f** 6
13	**1f**	**4k**	6 + NBu_4Br	47	**2f** 43
14	**1f**	**4l**	6	86	**2f** 85
15	**1e**	**4l**	6	82	**2e** 81
16	**1f**	**4f**	6	>89	**2f** 89
17	**1e**	**4f**	6	76	**2e** 75
18	**1f**	**4h**	6	3	**2f** 2
19	**1f**	**4g**	6	22	**2f** 21

[a] Reaction conditions: 80 °C, 15 h, amine : base molar ratio 10 : 1, base conc. 0.067 mol dm^{-3}, NBu_4Br : base molar ratio = 2 : 1, 1.5 ml water. [b] By GLC based on the starting acetylenic amine.



effective than one probably because, even in a transient way, they can reinforce the hydrophobic assembly against the interference of water. With **1f**, however, which has an *N*-benzyl group in place of an *N*-*n*-butyl the effect is less apparent (entries 18 and 19 of Table 5) because of the higher hydrophobicity of the former. In the homogeneous solution in acetonitrile two hydrogen bonds tend to hamper the subsequent reaction of the carbamate anion with the triple bond by reducing its nucleophilicity, and so one hydrogen bridge turns out to be better. The situation appears to be more complex than suggested by the above interpretation, however. In fact when two protons (plus one coming from protonation) are present in certain bases such as in **4k** and **4g** the reaction in the presence of water gives poor results (Table 6, entries 12 and 19), while excellent results are obtained in acetonitrile (Table 1, entries 9 and 16). In the former case it is likely that solubility in water becomes too high (as with guanidines containing short allkyl chains) and this is confirmed by the fact that **4l** and **4f** which have similar structure but possess a long aliphatic chain instead of a cyclohexyl group the yield is high again (Table 6, entries 14 and 16). In the latter case (reaction in acetonitrile) it is possible that more efficient catalysis is exerted by the formation of more complex aggregates held by additional hydrogen bonds. This is only a hypothesis, however, which requires further investigation. Hydrogen bonds are known to stabilize transition states in enzyme reactions.[10] Hamilton[11] has reported such interactions in hydrophobic systems. We are not able at present to estimate the extent to which hydrogen bonds in our hydrophobic system can facilitate the formation of oxazolidinones. Even transient interactions could have significant effects, however, as observed experimentally. Studies are in progress aimed at ascertaining the influence of hydrogen bonds and of other factors on the size and tightness of the molecular assembly involved and its reactivity.

Experimental

Mps were determined on an Electrothermal melting point apparatus and are uncorrected. Elemental analyses were carried out with a Carlo Erba Elemental Analyser Model EA 1108. Infrared spectra were recorded with a Nicolet 5PCFT-IR spectrophotometer. Mass spectra were obtained using a Hewlett Packard Mass Selective Detector 5971 Series interfaced with a Hewlett Packard 5890 Series II GC or a FinniganMat SSQ 710 spectrometer both at 70 eV ionising voltage. ^{1}H NMR spectra were recorded at 300 MHz and ^{13}C NMR spectra at 75 MHz on a Bruker AC 300 spectrometer with Me_4Si as an internal reference. Chemical shifts and coupling constants (J) are given as δ values (ppm) and in Hz respectively. The reaction mixtures were analysed by GLC using a capillary column with methylsilicone (OV101) as stationary phase or by TLC (SiO_2). Quantitative determinations were carried out by GLC using the internal standard method or by weighing the isolated products. Merck silica gel 60 (60–230 mesh) was used for column chromatography. Analytical TLC plates and silica gel 60F 254 was purchased from Merck. *N*-Methylprop-2-ynamine **1a**, 1,1-dimethylprop-2-ynamine, prop-2-yn-1-ol, 2-methylbut-3-yn-2-ol, and but-3-yn-2-ol are commercial products (Aldrich, Acros-Carlo Erba). Acetonitrile was dried over 3 Å molecular sieves. Alkyl and cycloalkyl primary amines, piperidine, tetramethylurea, diisopropylurea, dicyclohexylcarbodiimide, diisopropylcarbodiimide, triphosgene, **4a**, **4i**, **5a**, **5b**, **6**, **7**, **10** and **11** are commercially available products (Aldrich, Fluka, Acros-Carlo Erba) and were used without further purification.

Synthesis of acetylenic amines

N-Butylprop-2-ynamine **1b**, *N*-benzylprop-2-ynamine **1c** and *N*-butyl-1-methylprop-2-ynamine **1d** were prepared by reaction of prop-2-ynyl toluene-*p*-sulfonate or 1-methylprop-2-ynyl toluene-*p*-sulfonate with the respective amine according to a procedure reported in the literature.[11] *N*-Butyl-1,1-dimethylprop-2-ynamine **1e**, *N*-hexyl-1,1-dimethylprop-2-ynamine **1g** and *N*-allyl-1,1-dimethylprop-2-ynamine **1h** were prepared from 1,1-dimethylprop-2-ynyl acetate and the respective amine according to the literature.[12] *N*-Benzyl-1,1-dimethylprop-2-ynamine **1f** was prepared according to the conventional procedure of alkylation of primary amines with alkyl halides. Thus an excess of 1,1-dimethylprop-2-ynamine (13 g, 160 mmol) was allowed to react with benzyl chloride (7 g, 60 mmol) in dry THF (50 ml) at 60 °C for 15 h. A white solid (mp 47 °C, 6.5 g, 63%) was recovered after acid-base extraction. *N*-Benzylbut-2-ynamine **1i** was prepared from 1-bromobut-2-yne and benzylamine as reported in the literature.[11]

Synthesis of substituted guanidines

Alkylureas (1,1,3,3-tetraoctylurea and 1,3-diisopropylurea) were prepared from triphosgene and the respective amine, adapting literature[13] methods. Thus triphosgene (2.0 g, 7 mmol) and dry dichloromethane (20 ml) were charged to a 100 ml two-necked flask and a solution of ethyldiisopropylamine (4.5 ml, 25 mmol) and piperidine (5.0 ml, 50 mmol) in dry dichloromethane (20 ml) was added slowly at room temperature under a nitrogen atmosphere. After heating at 40 °C for 24 h the solvent was removed under reduced pressure. 1,3-Dipiperidylurea was isolated (2.7 g, 76%) as a white solid (mp 74 °C) by acid extraction of the basic products (Found: C, 67.2; H, 10.1; N, 14.2. $C_{11}H_{20}H_2O$ requires C, 67.3; H, 10.2; N, 14.3%).

Guanidines **4b–g** and **9** were also prepared by modifying the literature procedures.[14] An illustrative example is given for the synthesis of 2-cyclohexyl-1,1,3,3-tetramethylguanidine **4e**. Dry 1,2-dichloroethane (50 ml) and tetramethylurea (5.05 ml, 42 mmol) were charged to a 250 ml two-necked flask and oxalyl chloride (8.0 ml, 92.0 mmol) was added at room temperature. The solution was heated at 60 °C for 12 h, then the solvent was removed under vacuum. The residual yellow solid was dissolved in dry acetonitrile (30 ml), and cyclohexylamine (9.2 ml, 80.6 mmol) in dry acetonitrile (20 ml) was added dropwise at 0 °C. The reaction mixture was allowed to warm to room temperature and then refluxed for 24 h. After removal of the sol-

vent under reduced pressure the residue was treated with 30% aqueous NaOH. The organic layer was extracted with diethyl ether and dried with anhydrous Na_2SO_4. After removal of the diethyl ether, distillation of the residue at 120 °C/6 mbar yielded a colorless oil (6.5 g, 76%) (Found: C, 66.6; H, 11.6; N, 21.0. $C_{11}H_{23}N_3$ requires C, 67.0; H, 11.7; N, 21.3%).

Guanidines **4h**, **k**, **l** and **8** were prepared according to a different literature procedure.[15] Thus for 1,2,3-tricyclohexylguanidine **4l**, 1,3-dicyclohexylcarbodiimide (4.2 g, 20 mmol) and cyclohexylamine (4.6 g, 40 mmol) were charged with dry *tert*-butyl alcohol (40 ml) in a 250 ml two-necked flask equipped with a reflux condenser and a nitrogen inlet tube. The mixture was stirred under a nitrogen atmosphere at 100 °C for 24 h. After removal of the solvent under reduced pressure the residue was distilled first at 90 °C/15 mbar to remove unconverted cyclohexylamine then at 170 °C/1 mbar,† thus obtaining pure guanidine (4.5 g, 74%) as a white solid (mp 92 °C) (Found: C, 74.6; H, 11.4; N, 13.7. $C_{19}H_{35}N_3$ requires C, 74.8; H, 11.5; N, 13.8%). All the superbases were kept under nitrogen.

General procedure for the synthesis of oxazolidinones from acetylenic amines and carbon dioxide

Reactions under CO_2 pressure in acetonitrile or water

Catalytic and stoichiometric carboxylations were carried out in a 40 cm^3 stainless steel autoclave (Parr) with magnetic stirring. In a typical experiment the autoclave was charged under nitrogen with the superbase and the amine in the appropriate ratio. A fixed volume of solvent (acetonitrile) was added in order to obtain the required concentration of the base. The autoclave was cooled at about −10 °C, purged four times with CO_2, then pressurised with CO_2 and heated under stirring for the required time. Conditions are indicated in Tables 1, 2 and 3. Reactions with water in place of acetonitrile were carried out similarly (conditions in Table 4).

For reactions at atmospheric pressure a Schlenk glass reactor (50 ml) with magnetic stirring was utilized. In a typical experiment the reactor was charged under nitrogen with the superbase and the amine in the appropriate ratio. A fixed volume of water was added and CO_2 was released through the reactor for some minutes, then the mixture was heated at 70 °C and stirred under an atmosphere of CO_2 for 24 h. Conditions are indicated in Table 6.

Reactions with sodium hydrogen carbonate as carbon dioxide carrier

The reactions were carried out in a Schlenk glass reactor (50 ml) with magnetic stirring. In a typical experiment the reactor was charged under nitrogen with the superbase, the amine, sodium hydrogen carbonate and where indicated with NBu_4Br in the appropriate ratio. A fixed volume of acetonitrile or water was added. The mixture was heated at 80 °C under stirring for 15 h. Conditions are indicated in Tables 4 and 6.

Separation of the products

Pure oxazolidinones **2a**–**i** and **3f** were isolated from the reaction mixture in acetonitrile by evaporating the solvent and removing the basic compounds by acid extraction. Separation of **2** and **3** was carried out by column chromatography on silica gel with hexane–ethyl acetate (8 : 2) as eluent.

Characterization of guanidines

New guanidines were identified by elemental analysis, IR, ^1H NMR and MS data.

2-*n*-Propyl-1,1,3,3-tetramethylguanidine 4b. Colourless oil (Found: C, 60.9; H, 12.0; N, 26.7. $C_8H_{19}N_3$ requires C, 61.1; H, 12.1; N, 26.8%); ν_{max}(film)/cm^{-1} 2968m, 2938m, 1618s, 1440vs, 867m; δ_H 0.84 (3H, t, *J* 7.2, Me), 1.43–1.53 (2H, m, CH_2), 2.61 (6H, s, 2Me), 2.69 (6H, s, 2Me), 3.02 (2H, t, *J* 7.2, CH_2); *m*/*z* 157 (M^+, 22%), 113 (17), 85 (76), 71 (100), 42 (29).

2-*n*-Octyl-1,1,3,3-tetramethylguanidine 4c. Pale yellow oil (Found: C, 68.6; H, 12.8; N, 18.4. $C_{13}H_{29}N_3$ requires C, 68.7; H, 12.8; N, 18.5%); ν_{max}(film)/cm^{-1} 2924s, 2854m, 1624s, 1447vs, 867w; δ_H 0.75 (3H, t, *J* 7.1, Me), 1.14 (10 H, br s, $5CH_2$), 1.34–1.41 (2H, m, CH_2), 2.52 (6H, s, 2Me), 2.61 (6H, s, 2Me), 2.98 (2H, t, *J* 7.3, CH_2); *m*/*z* 227 (M^+, 23%), 198 (11), 184 (14), 168 (17), 142 (10), 100 (25), 85 (81), 71 (100).

2-*n*-Dodecyl-1,1,3,3-tetramethylguanidine 4d. Deliquescent pale yellow solid (Found: C, 72.0; H, 13.0; N, 14.7. $C_{17}H_{37}N_3$ requires C, 72.1; H, 13.1; N, 14.8%); ν_{max}(film)/cm^{-1} 2923vs, 2853s, 1623s, 1459s, 1358m; δ_H 0.87 (3H, t, *J* 6.9, Me), 1.24 (20H, br s, $10CH_2$), 2.78 (12H, br s, 4Me), 3.11 (2H, t, *J* 7.1, CH_2); *m*/*z* 283 (M^+, 5%), 239 (4), 196 (7), 184 (6), 142 (6), 115 (7), 100 (18), 85 (67), 71 (100), 43 (34).

2-Cyclohexyl-1,1,3,3-tetramethylguanidine 4e. Pale yellow oil (Found: C, 68.8; H, 11.6; N, 21.1. $C_{11}H_{23}N_3$ requires C, 67.0; H, 11.7; N, 21.3%); ν_{max}(film)/cm^{-1} 2926s, 2853m, 1620s, 1450s, 1362m, 1125w, 1013w, 868w; δ_H 1.19–1.48 (6H, m, $3CH_2$), 1.55–1.75 (4H, m, $2CH_2$), 2.72 (6H, s, 2Me), 2.74 (6H, s, 2Me), 3.03–3.12 (1H, m, CH); *m*/*z* 197 (M^+, 8%), 154 (10), 126 (7), 111 (11), 100 (13), 85 (23), 71 (100).

2-*n*-Dodecyl-1,3-diisopropylguanidine 4f. Deliquescent white solid (Found: C, 73.2; H, 13.2; N, 13.4. $C_{19}H_{41}N_3$ requires C, 73.3; H, 13.2; N, 13.5%); ν_{max}(film)/cm^{-1} 3249s, 3238s, 2945m, 2926, 2855s, 1619vs, 1468m, 1371m, 1170w; δ_H 0.87 (3H, t, *J* 7.1, Me), 1.10 (12H, d, *J* 6.3, 4Me), 1.24 (20H, br s, $10CH_2$), 1.88, 1.92 (2H, 2 br s, 2NH), 2.98 (2H, t, *J* 7.1, CH_2), 3.44–3.64 (2H, m, 2CH); *m*/*z* 311 (M^+, 9%), 296 (9), 212 (11), 200 (18), 170 (19), 156 (16), 85 (27), 58 (100), 43 (96).

2-Cyclohexyl-1,3-diisopropylguanidine 4g. Deliquescent white solid (Found: C, 69.2; H, 12.0; N, 18.6. $C_{13}H_{27}N_3$ requires C, 69.3; H, 12.0; N, 18.7%); ν_{max}(film)/cm^{-1} 3345m, 2942s, 2929vs, 2854s, 1643vs, 1499m, 1450s, 1363m, 1176m, 1125w, 889w; δ_H 1.07 (12H, d, *J* 6.4, 4Me), 1.11–1.32 (6H, m, $3CH_2$), 1.54–1.58, 1.66–1.71 (4H, 2 m, $2CH_2$), 1.81, 1.85 (2H, 2 br s, 2NH); *m*/*z* 225 (M^+, 5%), 210 (3), 182 (7), 110 (11), 98 (32), 85 (29), 58 (199), 43 (98).

1,2,3-Triisopropylguanidine 4h. Deliquescent pale yellow solid (Found: C, 64.8; H, 12.4; N, 22.6. $C_{10}H_{23}N_3$ requires C, 64.9; H, 12.4; N, 22.7%); ν_{max}(film)/cm^{-1} 3212w, 3174m, 3110m, 2970m, 1618s, 1443vs, 1378m, 1339w, 1169w, 867w; δ_H 1.10 (18H, d, *J* 6.4, 6Me), 1.90, 1.95 (2H, 2 br s, 2NH), 3.44–3.53 (3H, m, 3CH); *m*/*z* 185 (M^+, 7%), 170 (5), 128 (9), 113 (14), 85 (36), 69 (24), 58 (96), 43 (100).

1,2,3-Tricyclohexylguanidine 4k. White solid, mp 92 °C (Found: C, 74.7; H, 11.5; N, 13.7. $C_{19}H_{35}N_3$ requires C, 74.8; H, 11.5; N, 13.8%); ν_{max}(KBr)/cm^{-1} 3310s, 3241s, 2924vs, 2850s, 1625s, 1622vs, 1530s, 1510s, 1448s, 1249m, 889m, 723m; δ_H 1.11–1.37 (18H, m, 18CH), 1.56–1.61, 1.69–1.75 (12H, 2 m, 12CH), 1.83, 1.88 (2H, 2 br s, 2NH), 3.09–3.17 (3H, m, 3CH); *m*/*z* 305 (M^+, 8%), 223 (5), 166 (9), 162 (7), 141 (38), 110 (21), 98 (85), 83 (24), 55 (100), 41 (65).

2-*n*-Dodecyl-1,3-dicyclohexylguanidine 4l. Colourless oil (Found: C, 76.6; H, 12.4; N, 10.6. $C_{25}H_{49}N_3$ requires C, 76.7; H, 12.5; N, 10.7%); ν_{max}(film)/cm^{-1} 3306m, 2925vs, 2853s, 1644s, 1501m, 1449vs, 1337m, 1148m, 889m, 720w; δ_H 0.86 (3H, t, *J* 7.0, Me), 1.07–1.20 (6H, m, 6CH), 1.23 (18H, br s, $9CH_2$), 1.23–1.35 (8H, m, 8CH), 1.46–1.58 (4H, m, 4CH), 1.67–1.71 (4H, m, 4CH), 1.87, 1.89 (2H, br s, 2NH), 2.97 (2H, t, *J* 7.3, CH_2), 3.05–3.16 (2H, m, 2CH); *m*/*z* (CI) 392 [(M + 1)$^+$, 61%], 391 (M^+, 100), 311 (42), 310 (46), 294 (44), 207 (67).

***N*,*N*′-Dicyclohexylpiperidine-1-carboximidamide 8.** White solid, mp 40 °C (Found: C, 74.1; H, 11.3; N, 14.3. $C_{18}H_{33}N_3$ requires C, 74.2; H, 11.3; N, 14.4%); ν_{max}(KBr)/cm^{-1} 3408m, 2927vs, 3850s, 1634vs, 1448m, 1365m, 1251m, 1115w, 1047w, 890w; δ_H 1.13–1.29 (12H, m, 12CH), 1.52 (6H, br s, $3CH_2$), 1.57–1.61, 1.71–1.75 (8H, 2 m, $4CH_2$), 1.89 (1H, br s, NH),

† 1 Bar = 10^5 Pa.

2.85–2.95 (2H, m, 2CH), 3.01–3.03 (4H, m, $2CH_2$); *m/z* 291 (M^+, 12%), 248 (13), 127 (58), 84 (100), 55 (45).

***N*-Cyclohexyl-1,1-di(piperidin-1-yl)methylidenamine 9.** Pale yellow oil (Found: C, 73.5; H, 11.2; N, 151. $C_{17}H_{31}N_3$ requires C, 73.6; H, 11.2; N, 15.2%); ν_{max}(film)/cm^{-1} 2927s, 2852m, 1616s, 1446vs, 1370s, 1249w, 1128w, 866w; δ_H 1.14–1.34 (6H, m, $3CH_2$) 1.50, 1.54 (12H, 2 br s, $6CH_2$), 1.54–1.62, 1.67–1.73 (4H, 2 m, $2CH_2$), 2.99–3.04 (8H, m, $4CH_2$), 3.13–3.18 (1H, m, CH); *m/z* 277 (M^+, 19%), 234 (18), 194 (20), 151 (22), 111 (100), 84 (84), 69 (21), 55 (40), 41 (36).

Characterization of products

Spectroscopic data for the identification of products **2f** and **3f** have been reported.[1] New compounds were identified by elemental analysis, IR, ^1H, ^{13}C NMR and MS data.

***N*-Methyl-5-methylene-1,3-oxazolidin-2-one 2a.** Colourless oil (Found: C, 53.1; H, 6.2; N, 12.3. $C_5H_7NO_2$ requires C, 53.1; H, 6.2; N, 12.4%); ν_{max}(film)/cm^{-1} 2929m, 1791vs, 1680s, 1488m, 1383m, 1245m, 954w, 876w, 756m; δ_H 2.85 (3H, s, Me), 4.11 (2H, t, *J* 2.5, CH_2), 4.22 (1H, dt, *J* 2.8, 2.7, =C*H*H), 4.64 (1H, dt, *J* 2.8, 2.7, =CH*H*); *m/z* 113 (M^+, 100%), 98 (2), 85 (10), 69 (5), 57 (20), 42 (20).

***N*-Butyl-5-methylene-1,3-oxazolidin-2-one 2b.** Colourless oil (Found: C, 61.8; H, 8.4; N, 8.9. $C_8H_{13}NO_2$ requires C, 61.9; H, 8.4; N, 9.0%); ν_{max}(film)/cm^{-1} 2963m, 2932m, 2872m, 1781s, 1691m, 1473m, 1427m, 1283m, 1236w, 1115w, 1047m, 829w; δ_H 0.93 (3H, t, *J* 7.4, Me), 1.28–1.40 (2H, m, CH_2), 1.48–1.58 (2H, m, CH_2), 3.29 (2H, t, *J* 7.3, CH_2), 4.14 (2H, t, *J* 2.4, CH_2), 4.26 (1H, dd, *J* 2.4, 2.3, =CH), 4.72 (1H, dd, *J* 2.4, 2.4, =CH); δ_C 13.52 (Me), 19.74 (CH_2), 29.29 (CH_2), 43.51 (CH_2), 47.81 (CH_2), 86.17 (=CH_2), 149.24 (=C), 155.52 (CO); *m/z* 155 (M^+, 23%), 126 (3), 112 (37), 84 (12), 57 (25), 41 (100).

***N*-Benzyl-5-methylene-1,3-oxazolidin-2-one 2c.** Colourless oil (Found: C, 68.7; H, 5.8; N, 7.3. $C_{11}H_{11}NO_2$ requires C, 68.8; H, 5.8; N, 7.4%); ν_{max}(film)/cm^{-1} 3064m, 3032m, 2925w, 1794s, 1679s, 1425m, 1282m, 1239m, 1059m, 970w, 877w, 834w; δ_H 4.01 (2H, t, *J* 2.4, CH_2), 4.22 (1H, dd, *J* 2.9, 2.4, =CH), 4.46 (2H, s, CH_2), 4.73 (1H, dd, *J* 2.9, 2.4, =CH), 7.04–7.19 (5H, m, Ph); δ_C 47.27 (CH_2), 86.62 (=CH_2), 128.15 (2 =CH), 128.20 (=CH), 128.96 (2 =CH), 135.07 (qC), 149.07 (qC), 155.62 (CO); *m/z* 189 (M^+, 5%), 91 (100), 65 (19), 51 (6).

***N*-Butyl-4-methyl-5-methylene-1,3-oxazolidin-2-one 2d.** Colourless oil (Found: C, 63.8; H, 8.8; N, 8.2. $C_9H_{15}NO_2$ requires C, 63.9; H, 8.9; N, 8.3%); ν_{max}(film)/cm^{-1} 2962s, 2875s, 1781vs, 1695s, 1447m, 1418m, 1379w, 1283s, 1224m, 1084s, 1034s, 958m; δ_H 0.92 (3H, t, *J* 7.3, Me), 1.26–1.37 (2H, m, CH_2), 1.37 (3H, d, *J* 6.4, Me), 1.46–1.54 (2H, m, CH_2), 3.06 (1H, dddd, *J* 14.2, 8.4, 5.4, 1.4, NCH*H*), 3.43 (1H, dddd, *J* 14.2, 8.6, 7.4, 1.3, NC*H*H), 4.22 (1H, dd, *J* 3.2, 2.7, =CH), 4.36 (1H, qdd, *J* 6.4, 2.7, 1.3, =CH), 4.68 (1H, dd, *J* 3.2, 1.3, =CH); *m/z* 169 (M^+, 10%), 154 (21), 140 (5), 125 (4), 110 (29), 82 (100), 68 (9), 54 (6).

***N*-Butyl-4,4-dimethyl-5-methylene-1,3-oxazolidin-2-one 2e.** Colourless oil (Found: C, 65.6; H, 9.3; N, 7.6. $C_{10}H_{17}NO_2$ requires C, 65.7; H, 9.3; N, 7.7%); ν_{max}(film)/cm^{-1} 2962s, 2936s, 2875m, 1777vs, 1674s, 1444m, 1260w, 1110s, 1034s, 830m; δ_H 0.90 (3H, t, *J* 7.3, Me), 1.27–1.31 (2H, m, CH_2), 1.38 (6H, s, 2 Me), 1.53–1.59 (2H, m, CH_2), 3.10 (2H, t, *J* 7.9, CH_2), 4.18 (1H, d, *J* 3.2, =C*H*H), 4.59 (1H, d, *J* 3.2, =CH*H*); *m/z* 183 (M^+, 5%), 169 (100), 154 (5), 140 (10), 126 (5), 112 (80), 98 (10).

***N*-Hexyl-4,4-dimethyl-5-methylene-1,3-oxazolidin-2-one 2g.** Colourless oil (Found: C, 68.1; H, 9.9; N, 6.5. $C_{12}H_{21}NO_2$ requires C, 68.2; H, 10.0; N, 6.6%); ν_{max}(film)/cm^{-1} 2960s, 2932s, 2869m, 1773vs, 1675s, 1439m, 1260w, 1116s, 829m, 764m; δ_H 0.89 (3H, t, *J* 6.8, Me), 1.25–1.32 (6H, m, $3CH_2$), 1.41 (6H, s, 2Me), 1.58–1.62 (2H, m, CH_2), 3.12 (2H, t, *J* 7.7, NCH_2), 4.19 (1H, d, *J* 3.3, =CH), 4.62 (1H, d, *J* 3.3, =CH); *m/z* 211 (M^+, 6%), 196 (100), 140 (14), 112 (65), 41 (21).

***N*-Allyl-4,4-dimethyl-5-methylene-1,3-oxazolidin-2-one 2h.** Colourless oil (Found: C, 64.6; H, 7.7; N, 8.3. $C_9H_{13}NO_2$ requires C, 64.7; H, 7.8; N, 8.4%); ν_{max}(film)/cm^{-1} 2980s, 2934m, 1776vs, 1675s, 1430m, 1400s, 1330m, 1047s, 980m, 760m; δ_H 1.37 (6H, s, 2Me), 3.80 (2H, ddd, *J* 6.0, 1.4, 1.3, CH_2), 4.19 (1H, d, *J* 3.2, =CH), 4.59 (1H, d, *J* 3.2, =CH), 5.11 (1H, ddt, *J* 10.1, 1.4, 1.3, =CH*H*), 5.20 (1H, *J* 17.1, 1.4, 1.3, C*H*H), 5.73–5.85 (1H, m, =CH); δ_C 27.38 (2Me), 42.79 (CH_2), 61.26 (qC), 83.85 (=CH_2), 117.38 (=CH_2), 133.55 (=CH), 154.80 (qC), 160.60 (qC); *m/z* 167 (M^+, 10%), 152 (100), 140 (6), 124 (5), 112 (11), 82 (10), 56 (7).

***N*-Benzyl-5-ethylidene-1,3-oxazolidin-2-one 2i.** Pale yellow oil (Found: C, 70.8; H, 6.3; N, 6.8. $C_{12}H_{13}NO_2$ requires C, 70.9; H, 6.4; N, 6.9%); ν_{max}(film)/cm^{-1} 2923m, 2855w, 1783s, 1718s, 1646m, 1535w, 1479m, 1428m, 1208m, 1084s, 1000m, 755w, 702m; δ_H 1.65 (3H, dt, *J* 7.1, 2.3, Me), 3.92–3.97 (2H, m, CH_2), 4.43 (2H, s, CH_2), 4.25–4.57 (1H, m, =CH), 7.23–7.34 (5H, m, Ph); *m/z* 203 (M^+, 18%), 188 (2), 147 (51), 112, (4), 91 (100), 65 (6).

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