# The [2,3] sigmatropic rearrangement of *N*-benzyl-*O*-allylhydroxylamines

**Stephen G. Davies,* John F. Fox, Simon Jones, Anne J. Price, Miguel A. Sanz, Thomas G. R. Sellers, Andrew D. Smith and Fátima C. Teixeira**

*The Dyson Perrins Laboratory, University of Oxford, South Parks Road, Oxford, UK OX1 3QY*

***Received (in Cambridge, UK) 31st May 2002, Accepted 19th June 2002***
***First published as an Advance Article on the web 12th July 2002***

The rearrangement of a range of *N*-benzyl-*O*-allylhydroxylamines to the corresponding *N*-allylhydroxylamines upon treatment with *n*-BuLi in THF, followed by reduction to the corresponding *N*-allylamines, is described. Mechanistic studies of the transformation are consistent with an intramolecular [2,3] sigmatropic rearrangement.

## Introduction

Sigmatropic rearrangement processes have been used extensively within organic synthesis for a variety of synthetic applications. Of the many rearrangement processes that exist,[1] [2,3] sigmatropic rearrangements have received considerable attention as a method for carbon–carbon and carbon–heteroatom bond formation.[2] A variety of substrates have been shown to undergo this transformation,[3] including the Sommelet–Hauser rearrangement of quaternary ammonium salts,[4] the Meisenheimer rearrangement of tertiary amine oxides,[5] the Mislow rearrangement of allylic sulfoxides[6] and the related Wittig and aza-Wittig rearrangements of allylic ethers[7] and amines[8] (Fig. 1).

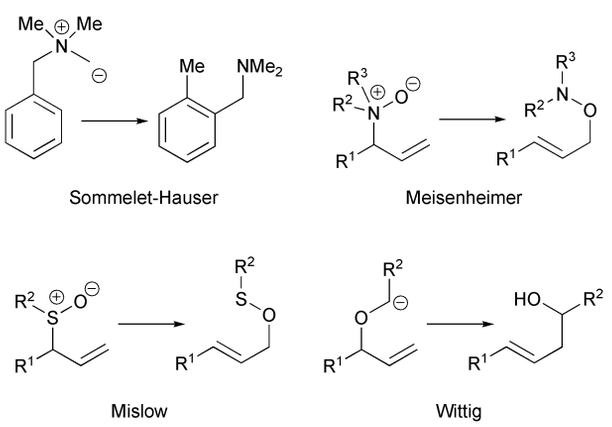



**Fig. 1** [2,3] Sigmatropic rearrangements.

As a result of the synthetic utility of these transformations,[9] there is an ongoing demand for novel rearrangement processes that facilitate the preparation of highly functionalised intermediates. During our investigations concerning the preparation of homochiral hydroxylamine chromium tricarbonyl complexes,[10] and the continuation of our lithium amide studies[11] we noticed an unusual rearrangement of *N*-benzyl-*O*-allylhydroxylamines such as **1** to the corresponding *N*-benzyl-*N*-allylhydroxylamines **2**. This process was assumed to arise from an intramolecular [2,3] sigmatropic rearrangement, formally analogous to the [2,3] Wittig rearrangement. Related processes have been reported in the literature, notably involving the rearrangement of allyl oxime ethers to nitrones under both thermal[12,13] and palladium(II) catalyzed conditions,[14] while the reverse rearrangement of *N*-aryl-*N*-allylhydroxylamines **3** to *O*-allylhydroxylamines **4** has also been recently communicated (Fig. 2).[15]

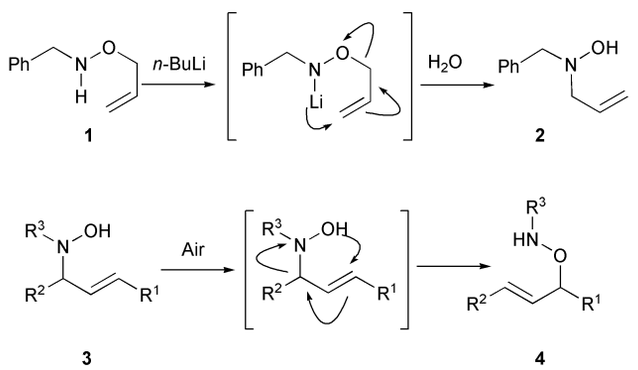



**Fig. 2** [2,3] Sigmatropic *N*,*O* rearrangements.

The recent rediscovery[16,17] of this novel *N*,*O* [2,3] sigmatropic rearrangement protocol, which we first reported four years ago,[18] has prompted us to report herein our full mechanistic investigations concerning the [2,3] sigmatropic rearrangement of *N*-benzyl-*O*-allylhydroxylamines to *N*-benzyl-*N*-allylhydroxylamines.

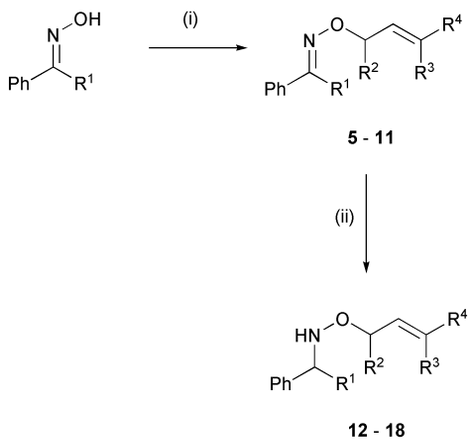
## Results and discussion

### Preparation of *N*-benzyl-*O*-allylhydroxylamine substrates

To investigate fully the substrate limitations of this rearrangement, an efficient route for the preparation of a range of substituted *N*,*O*-disubstituted hydroxylamines was required. The most widely used approach for the synthesis of such substrates involves the reduction of *O*-substituted oximes, which in turn may be readily prepared by *O*-alkylation of oximes.[19] In this manner, treatment of benzaldehyde oxime with KO$^t$Bu in THF and subsequent alkylation with either allyl, crotyl†, 3-methylbut-2-enyl, (*E*)-cinnamyl, 1-methylallyl or 1-methylbut-2-enyl halides respectively gave the *O*-allyl oximes **5**–**10** in good to excellent yields after purification by distillation or chromatography.[20] Although *O*-cinnamyl oxime **8** was isolated as a single geometric isomer using this alkylation protocol, the crotyl and 1-methyl-but-2-enyl bromides were

† The IUPAC name for crotyl is but-2-enyl.

supplied as 76 : 24 or 83 : 17 mixtures of (*E*) and (*Z*) isomers respectively, and so **6** and **10** were isolated as a corresponding mixture of isomers. Similar treatment of acetophenone oxime with allyl bromide gave *O*-allyl oxime **11** in high yield. While a number of reducing agents have previously been employed for the reduction of oximes,[21,22] in our hands *O*-allyl oximes **5**–**11** were readily reduced with pyridine–borane, to give the desired *N*-benzyl-*O*-allylhydroxylamines **12**–**18** in excellent overall yields (Scheme 1).




| | $R^1$ | $R^2$ | $R^3$ | $R^4$ | Yield | | Yield |
|---|---|---|---|---|---|---|---|
| **5** | H | H | H | H | 91% | **12** | 94% |
| **6** | H | H | H/Me *E*/*Z* 76:24 | | 86% | **13** | 85% |
| **7** | H | H | Me | Me | 89% | **14** | 80% |
| **8** | H | H | H | Ph | 83% | **15** | 84% |
| **9** | H | Me | H | H | 68% | **16** | 69% |
| **10** | H | Me | H/Me *E*/*Z* 83:17 | | 43% | **17** | 82% |
| **11** | Me | H | H | H | 93% | **18** | 83% |

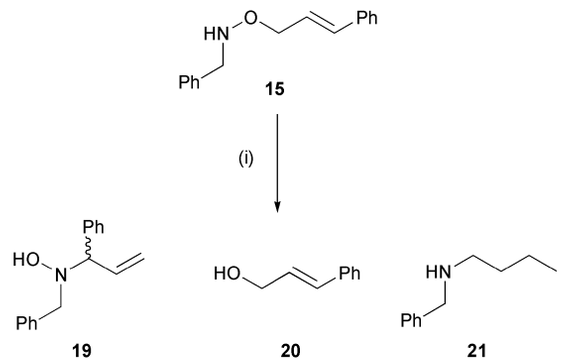
**Scheme 1** *Reagents and conditions*: (i) KO$^t$Bu, THF then alkyl halide; (ii) pyridine–borane (3 eq.), 0 °C to rt.

### [2,3] Sigmatropic rearrangements—initial investigations

With a range of *N*-benzyl-*O*-allylhydroxylamines **12**–**18** in hand, the optimal reaction conditions required for the rearrangement were investigated, with (*E*)-*N*-benzyl-*O*-(3-phenylallyl)hydroxylamine **15** initially used for model studies. Preliminary results used *n*-BuLi (1.1 eq.) at −78 °C to initiate the rearrangement, and toluene as the reaction solvent. Upon warming to rt, the total consumption of starting material was noted after 10 minutes. $^1$H NMR spectroscopic analysis of the crude reaction mixture showed a 1 : 1 : 1 mixture of three components, identified as the required rearrangement products *N*-benzyl-*N*-(1-phenylallyl)hydroxylamine **19**, cinnamyl alcohol **20** and *N*-benzyl-*N*-butylamine **21**.[23] *N*-Benzyl-*N*-butylamine **21** presumably arises from the direct displacement of the alkoxide group from the intermediate lithium amide with *n*-BuLi, an electrophilic amination protocol which has been extensively studied by Beak *et al*.[24] Indeed, treatment of hydroxylamine **15** with an excess (2 eq. and 10 eq.) of *n*-BuLi in toluene gave cinnamyl alcohol **20** and *N*-benzyl-*N*-butylamine **21** as the predominant products (71% and 83% respectively) over the rearrangement product **19** (29% and 17% respectively). However, exclusive formation of the rearrangement product **19** was noted if the rearrangement process was carried out with *n*-BuLi (1.1 eq.) in either THF or $Et_2O$ (Scheme 2).

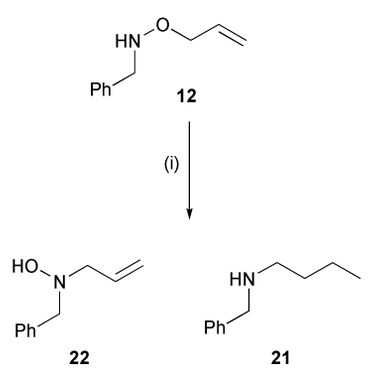
Similar treatment of *N*-benzyl-*O*-allylhydroxylamine **12** with 1.1 eq. *n*-BuLi showed predominant rearrangement to *N*-benzyl-*N*-allylhydroxylamine **22** in either toluene, THF or $Et_2O$, although *N*-benzyl-*N*-butylamine **21** was the major product observed upon addition of excess (5 eq. and 10 eq.) of *n*-BuLi in toluene (Scheme 3).

Further investigations concentrated upon identification of the optimal base required for activation of the rearrangement of (*E*)-*N*-benzyl-*O*-(3-phenylallyl)hydroxylamine **15** to




| Conditions | Solvent | 19 (%) | 20 (%) | 21 (%) |
|---|---|---|---|---|
| (i) | toluene | 50 | 50 | 50 |
| (ii) | toluene | 29 | 71 | 71 |
| (iii) | toluene | 17 | 83 | 83 |
| (i) | THF | 100 | 0 | 0 |
| (i) | $Et_2O$ | 100 | 0 | 0 |

**Scheme 2** *Reagents and conditions*: (i) *n*-BuLi (1.1 eq.), solvent, −78 °C to rt, 10 minutes; (ii) *n*-BuLi (2 eq.), solvent, −78 °C to rt, 10 minutes; (iii) *n*-BuLi (10 eq.), solvent, −78 °C to rt, 10 minutes.

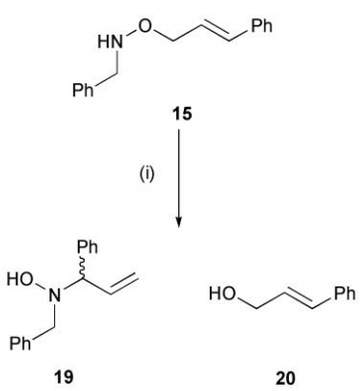



| Conditions | Solvent | 22 (%) | 21 (%) |
|---|---|---|---|
| (i) | toluene | 97 | 3 |
| (ii) | toluene | 11 | 89 |
| (iii) | toluene | 8 | 92 |
| (i) | THF | 100 | 0 |
| (i) | $Et_2O$ | 100 | 0 |

**Scheme 3** *Reagents and conditions*: (i) *n*-BuLi (1.1 eq.), solvent, −78 °C to rt, 10 minutes; (ii) *n*-BuLi (5 eq.), solvent, −78 °C to rt, 10 minutes; (iii) *n*-BuLi (10 eq.), solvent, −78 °C to rt, 10 minutes.

*N*-benzyl-*N*-(1-phenylallyl)hydroxylamine **19**, with MeMgBr or $^t$BuOK leading to significant substrate decomposition, and no isolable or identifiable products. *n*-BuLi was found to be essential to effect total and exclusive conversion to the rearrangement product **19**, while the use of LiHMDS or NaHMDS gave predominantly the rearrangement product **19**, but also significant quantities of cinnamyl alcohol **20** (Scheme 4).

Subsequent optimisation studies therefore used *n*-BuLi as the base and THF as the reaction solvent, and concentrated upon elucidating the effect of temperature on the rearrangement, using *N*-benzyl-*O*-allylhydroxylamine **12**. Thus, treatment of hydroxylamine **12** in THF with *n*-BuLi at either −78 °C, −61 °C, −43 °C, −20 °C or 0 °C for one hour prior to work-up indicated that the reaction had proceeded to 0%, 20%, 78%, >95% and >95% conversion respectively to *N*-benzyl-*N*-allylhydroxylamine **22**. Monitoring the extent of conversion of *N*-benzyl-*O*-allylhydroxylamine **12** to *N*-benzyl-*N*-allylhydroxylamine **22** with time at −43 °C showed that the reaction obeyed first order kinetics, with a rate constant $k$ = 0.024 min$^{-1}$ corresponding to a half life of the rearrangement of approximately 30 minutes. Further optimisation led to a more




| Base | 19 (%) | 20 (%) |
|---|---|---|
| *n*-BuLi | 100 | 0 |
| LiHMDS | 66 | 34 |
| NaHMDS | 88 | 12 |

**Scheme 4** *Reagents and conditions:* (i) base, THF, −78 °C to rt, 10 minutes.

convenient general reaction protocol, whereby deprotonation of amine **12** with *n*-BuLi at −78 °C for one hour, prior to warming to rt for 30 minutes, then addition of water gave the rearranged product in essentially quantitative conversion as determined by $^1$H NMR spectroscopic analysis.[25] Use of this optimised experimental procedure with hydroxylamine substrates **12**–**18** gave the rearranged products **19**, **22**–**27** as the sole reaction products in excellent conversion (>95%). The only problematic reaction of those studied was the attempted rearrangement of *N*-benzyl-*O*-(3-methylbut-2-enyl)hydroxylamine **14** involving rearrangement to a tertiary centre, which proceeded to give only 10% of the desired product **24**, even after deprotonation and stirring at rt for 48 h. However, by heating the reaction to reflux for 2 h after the initial addition of *n*-BuLi at −78 °C, the reaction could be driven to complete conversion to the desired hydroxylamine **24**. Attempted Kugelröhr distillation of the product *N*-benzyl-*N*-allylhydroxylamines resulted in extensive product decomposition, while purification by chromatography on silica typically gave <30% mass recovery. While unsatisfactory, the use of silica doped with 1% $NEt_3$ consistently furnished the best mass return (40% to 61% yield) of the purified hydroxylamines, although still in a noticeably lower isolated yield than that expected from the quantitative conversion observed from the $^1$H NMR spectrum of the crude material (Scheme 5).

Information regarding the transition state of this reaction was obtained from the rearrangement of *N*-benzyl-*O*-(1-methylallyl)hydroxylamine **16**, which results in the exclusive formation of (*E*)-*N*-benzyl-*N*-but-2-enylhydroxylamine **25**.[26] This is consistent with the reaction occurring *via* an envelope transition state, with the C(1) methyl group preferentially occupying a pseudo-equatorial position, consistent with that proposed for the related [2,3] Wittig rearrangement (Fig. 3).

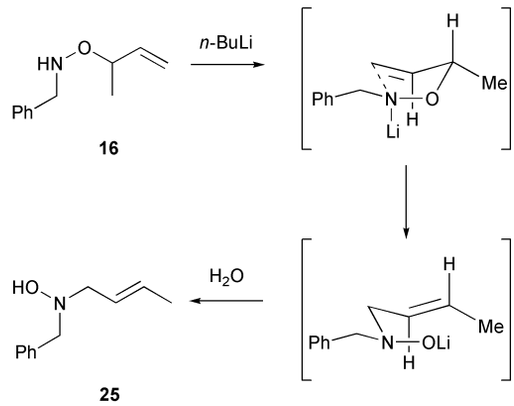



**Fig. 3**

## Reduction of hydroxylamine products

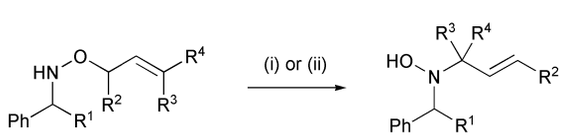
Although the rearrangement of hydroxylamines **12**–**18** had proceeded to excellent levels of conversion, the moderate isolated yields of compounds **19**, **22**–**27** were inadequate for practical preparative use. However, reduction of the *N*–*O* bond of hydroxylamines **19**, **22**–**27** could be easily performed using Zn and HCl to afford the corresponding allylic amines, which proved more amenable to purification. In this manner the desired allylic amines **28**–**34** were obtained in good to excellent yields and high purity (Scheme 6).

The success of this reduction protocol suggested that it would be convenient to perform the hydroxylamine reduction on the crude rearranged products. Thus, rearrangement of hydroxylamines **12**, **13** and **15** and direct reduction of the crude reaction mixture gave allylic amines **28**, **29** and **31** in excellent yields (91%, 93% and 92% respectively) over two steps (Scheme 7).

This 'one-pot' protocol involving rearrangement and direct reduction therefore provides a versatile route to α-functionalised allylic amines that have previously proved to be useful synthons in organic synthesis.[27]

## Further mechanistic investigations

Further mechanistic investigations were performed to confirm that the reaction was indeed a [2,3] rearrangement process, since the related rearrangement of *N*,*O*-disubstituted hydroxylamine

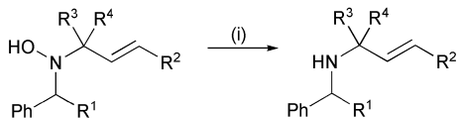



12 - 18 19, 22 - 27

| | Conditions | | Conversion* | $R^1$ | $R^2$ | $R^3$ | $R^4$ | Yield# |
|---|---|---|---|---|---|---|---|---|
| **12** | (i) | **22** | >95 | H | H | H | H | 61% |
| **13** | (i) | **23** | >95 | H | H | H/Me | | 59% |
| **14** | (ii) | **24** | >95 | H | H | Me | Me | 60% |
| **15** | (i) | **19** | >95 | H | H | H/Ph | | 40% |
| **16** | (i) | **25** | >95 | H | Me | H | H | 55% |
| **17** | (i) | **26** | >95 | H | Me | H/Me | | 55% |
| **18** | (i) | **27** | >95 | Me | H | H | H | 53% |

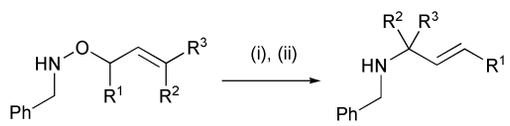
*As indicated by $^1$H NMR analysis of the crude reaction mixture.
# Isolated yields of hydroxylamines **19**, **22-27** after chromatography on silica doped with 1% $NEt_3$

**Scheme 5** *Reagents and conditions*: (i) *n*-BuLi, THF, −78 °C then rt; (ii) *n*-BuLi, THF, −78 °C then Δ.




| | $R^1$ | $R^2$ | $R^3$ | $R^4$ | | Yield |
|---|---|---|---|---|---|---|
| **22** | H | H | H | H | **28** | 90% |
| **23** | H | H | H/Me | | **29** | 94% |
| **24** | H | H | Me | Me | **30** | 92% |
| **19** | H | H | H/Ph | | **31** | 91% |
| **25** | H | Me | H | H | **32** | 70% |
| **26** | H | Me | H/Me | | **33** | 83% |
| **27** | Me | H | H | H | **34** | 94% |

**Scheme 6** *Reagents and conditions*: (i) Zn, HCl, 80 °C.




| | $R^1$ | $R^2$ | $R^3$ | | Yield |
|---|---|---|---|---|---|
| **12** | H | H | H | **28** | 91% |
| **13** | H | H/Me | | **29** | 93% |
| **15** | H | H/Ph | | **31** | 92% |

**Scheme 7** *Reagents and conditions*: (i) *n*-BuLi, THF, −78 °C then rt; (ii) Zn, HCl.

**35** to *N,N*-disubstituted hydroxylamine **37** has been shown to proceed *via* a [1,2] anionic process (Fig. 4).[28]

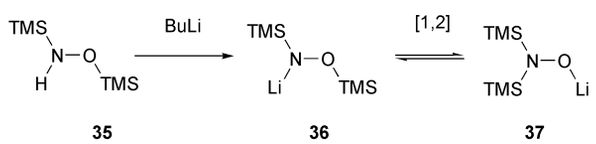



**Fig. 4**

However, for the rearrangement of hydroxylamines **12**–**18** this [1,2] type process was discounted, as the reaction of crotyl hydroxylamine **13** gave exclusively the [2,3] rearrangement product **23**. No trace of *N*-benzyl-*N*-crotylhydroxylamine **25**, the expected product arising from a [1,2] process, was observed in this reaction (Fig. 5).

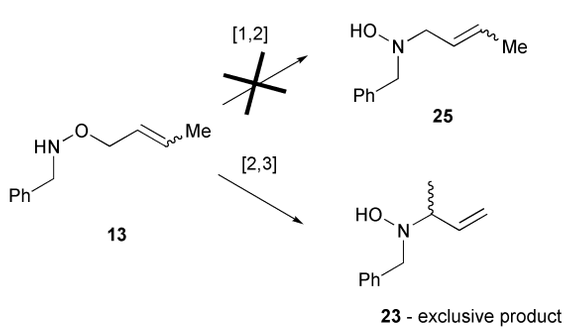
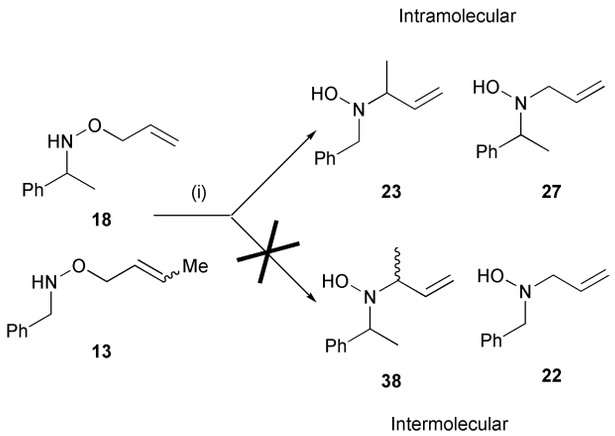



**Fig. 5**

The possibility of the mechanism proceeding either *via* an intermolecular rearrangement or dissociation of a radical pair was similarly ruled out by performing a crossover experiment with substrates **13** and **18**. Thus, an equimolar mixture of **13** and **18** was treated with 2 eq. of *n*-BuLi under the standard rearrangement conditions and the reaction mixture was analysed by $^1$H NMR spectroscopy. If an intermolecular process was occurring, rather than an intramolecular reaction, the scrambled products of rearrangement **22** and **38** would be observed alongside **23** and **27**. After isolation of the crude reaction mixture, only components **23** and **27** were observed, consistent with the respective intramolecular rearrangement processes, providing further convincing evidence that the mechanism of the reaction was an intramolecular [2,3] sigmatropic process (Scheme 8).




**Scheme 8** *Reagents and conditions*: (i) *n*-BuLi, THF, −78 °C then rt.

## Conclusion

In conclusion, a range of *N*-benzyl-*O*-allylhydroxylamines can be converted to the corresponding *N*-allylamines by a protocol consisting of an intramolecular [2,3] sigmatropic rearrangement and subsequent reduction with Zn and HCl. Further studies investigating diastereo- and enantioselective [2,3] sigmatropic *N–O* rearrangements are currently underway in our laboratory.

## Experimental

### General

All reactions described as being carried out under nitrogen were performed using standard vacuum line techniques, using glassware that was flame-dried. Reactions described as being performed at −78 °C were cooled by means of an acetone–dry ice bath, those at −61 °C by a chloroform slush bath, those at −43 °C by an acetonitrile slush bath, those at −20 °C by an ethylene glycol slush bath, and those at 0 °C by an ice bath. THF was distilled from sodium benzophenone ketyl under nitrogen prior to use. *n*-Butyllithium was used as a solution in hexanes and was titrated against diphenylacetic acid prior to use. All other reagents were used as supplied, without further purification. Column chromatography was performed on silica gel (Kieselgel 60), and neutral deactivated silica gel (Kieselgel 60, deactivated with 1% $NEt_3$). Thin layer chromatography was performed on Merck plates, either aluminium sheets coated with 0.2 mm silica gel 60 $F_{254}$, or glass plates coated with 0.25 mm silica gel 60 $F_{254}$. Plates were visualised either by UV light (254 nm), phosphomolybdic acid (10% in ethanol) or potassium permanganate (1% solution in 2% aqueous acetic acid, containing 7% potassium carbonate). Infra-red spectra were recorded using a Perkin-Elmer Paragon 1000 FT spectrometer. Selected peaks are reported. NMR spectra were recorded on Varian Gemini 200 ($^1$H 200 MHz, $^{13}$C 50 MHz), Bruker AC 200 ($^1$H 200 MHz, $^{13}$C 50 MHz), Bruker DPX 400 ($^1$H 400 MHz, $^{13}$C 100 MHz), Bruker AM 500 ($^1$H 500 MHz, $^{13}$C 125 MHz), or Bruker AMX 500 ($^1$H 500 MHz, $^{13}$C 125 MHz) spectrometers. Chemical shifts ($\delta_H$) are reported in parts per million and are referenced to the residual solvent peak. Coupling constants ($J$) are recorded in Hz. Low resolution mass spectra were recorded using a VG MASSLAB 20–250 instrument, with the major peaks listed with intensities quoted as percentages of the base peak. Accurate mass measurements were recorded on a VG Autospec instrument,

and were conducted by Mr R. Procter of the Dyson Perrins Laboratory. Retention times were recorded on a Pye 104 analytical GC, using nitrogen carrier gas (40 $cm^3$ $min^{-1}$). Peaks were detected by flame ionisation and are reported in minutes. Elemental analyses were obtained by Mr R. Prior of the Dyson Perrins analytical department on a Carla Erba 1106 combustion elemental analyser. Although compounds **8**, **9**, **11**, **12**, **18**, **19**, **22**, **29** and **33** have been noted previously in the literature, varying degrees of experimental data have been reported; full characterisation of these materials is described herein.

### General procedure for the preparation of *O*-allyl oximes

Potassium *tert*-butoxide (1 eq.) was added to a 0.1 M solution of oxime (1.1 eq.) in THF at 0 °C and stirred for 20 min under nitrogen. A solution of the allyl bromide (1.5 eq., 0.1 M in THF) was added *via* cannula to the resulting white suspension with stirring over 5 min, before warming to room temperature and stirring for a further hour. The resulting mixture was partitioned between distilled water and diethyl ether, the combined organic extracts dried ($MgSO_4$) and concentrated *in vacuo*. The resulting yellow oil was purified by short path distillation at reduced pressure, or column chromatography.

### Benzaldehyde *O*-allyloxime 5

From benzaldehyde oxime (5.00 g, 45.4 mmol) and allyl bromide (7.50 g, 62.0 mmol), the oxime **5** was obtained (6.03 g, 91%) as a colourless oil after short path distillation (bp 90 °C, 4 mmHg; lit.,[13] bp 90 °C, 8 mmHg); $\nu_{max}$/$cm^{-1}$ (film) 2921 (s), 1956 (w), 1880 (m), 1648 (m); $\delta_H$ (200 MHz, $CDCl_3$) 4.69 (2H, app dt, *J* 5.8, 1.4, OC$H_2$), 5.27 (1H, ddt, *J* 10.4, 1.7, 1.1, CH=C*H*H), 5.37 (1H, app dq, *J* 17.3, 1.6, CH=CH*H*), 6.07 (1H, ddt, *J* 17.3, 10.4, 5.8, C*H*=$CH_2$), 7.34–7.44 (3H, m, aromatic C*H*), 7.55–7.63 (2H, m, aromatic C*H*), 8.13 (1H, s, C*H*=N); $\delta_C$ (50 MHz, $CDCl_3$) 75.2 (*C*$H_2$O), 118.0 (*C*$H_2$=CH), 127.1, 128.8, 129.9 (aromatic *C*H), 132.3 (*ipso*-*C*), 134.2 ($CH_2$=*C*H), 148.9 (*C*H=N); *m*/*z* (APCI) ($MH^+$, 25%), 131 (65%), 106 (100%); HRMS calculated for $C_{10}H_{12}NO^+$: 162.0919. Found: 162.0922.

### Benzaldehyde *O*-(but-2-enyl)oxime 6

From benzaldehyde oxime (2.00 g, 16.5 mmol) and crotyl bromide (3.35 g, 24.8 mmol), the oxime **6** (2.28 g, 86%) was obtained as a colourless oil (*E* : *Z* 76 : 24) after short path distillation (bp 94 °C, 4 mmHg; lit.,[13] bp 52 °C, 0.5 mmHg); $\nu_{max}$/$cm^{-1}$ (film) 2917 (s), 1882 (w), 1674 (m); $\delta_H$ (500 MHz, $CDCl_3$) 1.76 (3H, dd, *J* 6.4, 1.2, C$H_3$), 4.63 (2H, d, *J* 6.5, (*E*)-OC$H_2$), 4.77 (2H, d, *J* 6.6, (*Z*)-OC$H_2$), 5.71–5.77 (1H, m, C*H*=CHC$H_3$), 5.82–5.87 (2H, m, CH=C*H*C$H_3$), 7.36–7.41 (3H, m, aromatic C*H*), 7.58–7.61 (2H, m, aromatic C*H*), 8.11 (1H, s, C*H*=N); $\delta_C$ (50 MHz, $CDCl_3$) 13.1 ((*Z*)-*C*$H_3$), 17.8 ((*E*)-*C*$H_3$), 69.6 ((*Z*)-*C*$H_2$), 75.1 ((*E*)-*C*$H_2$), 125.8, 126.8, 127.1, 127.2, 128.6, 128.8, 129.2, 129.9. 131.0 ((*E*)- and (*Z*)-aromatic *C*H and *C*H=*C*H), 132.5 (*ipso*-*C*), 148.8 (*C*H=N); *m*/*z* (APCI) 176 ($MH^+$, 15%), 122 (100%); HRMS calculated for $C_{11}H_{14}NO^+$: 176.1075. Found: 176.1074.

### Benzaldehyde *O*-(3-methylbut-2-enyl)oxime 7

From benzaldehyde oxime (2.00 g, 18.2 mmol) and 3-methylbut-2-enyl bromide (3.70 g, 24.8 mmol), the oxime **7** (2.78 g, 89%) was obtained as a colourless oil after short path distillation (bp 100–102 °C, 1 mmHg); $\nu_{max}$/$cm^{-1}$ (film) 2931 (s), 1954 (w), 1879 (w), 1812 (w), 1676 (s); $\delta_H$ (400 MHz, $CDCl_3$) 1.77 (3H, s, C$H_3$), 1.80 (3H, s, C$H_3$), 4.70 (2H, d, *J* 7.2, OC$H_2$), 5.50 (1H, tsept, *J* 7.2, 1.3, OC$H_2$C*H*), 7.36–7.41 (3H, m, aromatic C*H*), 7.56–7.60 (2H, m, aromatic C*H*), 8.10 (1H, s, C*H*=N); $\delta_C$ (50 MHz, $CDCl_3$) 18.1 (*C*$H_3$), 25.8 (*C*$H_3$), 70.9 (*C*$H_2$O), 120.1 (*C*H=C(C$H_3$)$_2$), 127.2, 128.9, 129.9 (aromatic *C*H), 132.7, 138.7 (*ipso*-*C* and CH=*C*(C$H_3$)$_2$), 148.7 (*C*H=N); *m*/*z* (APCI) 190 ($MH^+$, 5%), 122 (100%); HRMS calculated for $C_{12}H_{16}NO^+$: 190.1232. Found: 190.1239.

### (*E*)-Benzaldehyde *O*-(3-phenylallyl)oxime 8[29]

From benzaldehyde oxime (2.00 g, 16.5 mmol) and cinnamyl bromide (4.88 g, 24.8 mmol), the oxime **8** (3.25 g, 83%) was obtained as a colourless oil after column chromatography (1% $Et_2O$–hexane, $SiO_2$) which solidified on standing to give a cream coloured solid (mp 42–43 °C); $\nu_{max}$(film)/$cm^{-1}$ 3027 (s), 1952 (w), 1879 (w), 1810 (w); $\delta_H$ (200 MHz, $CDCl_3$) 5.02 (2H, dd, *J* 1.1, 6.1, C$H_2$CH=CH), 6.59 (1H, dt, *J* 16.0, 6.1, $CH_2$C*H*=CH), 6.85 (1H, d, *J* 16.0, $CH_2$CH=C*H*), 7.38–7.59 (8H, m, aromatic C*H*), 7.72–7.78 (2H, m, aromatic C*H*), 8.31 (1H, s, C*H*=N); $\delta_C$ (50 MHz, $CDCl_3$) 75.1 (*C*$H_2$CH=CH), 125.4, 126.8, 127.2, 128.0, 128.7, 128.8, 129.9, 133.5 (aromatic and alkene *C*H), 132.4, 136.8 (*ipso*-*C*), 149.0 (*C*H=N); *m*/*z* (APCI) 238 ($MH^+$, 5%), 117 (PhCH=C$HCH_2^+$, 100%); HRMS calculated for $C_{16}H_{15}NO$: C 81.0, H 6.4, N 5.9%. Found: C 80.8, H 6.4, N 5.75%.

### Benzaldehyde *O*-(1-methylallyl)oxime 9[30]

Benzaldehyde oxime (1.01 g, 8.34 mmol) and potassium *tert*-butoxide (1.02 g, 9.09 mmol) were dissolved in THF (40 ml). After stirring for 20 min, 3-chlorobut-1-ene (1.7 ml, 16.5 mmol) was added in a dropwise manner over five minutes. Sodium bromide (849 mg, 8.25 mmol) and tetrabutylammonium chloride (115 mg, 0.41 mmol) were then added, and the mixture refluxed for 18 h. After cooling, water (40 ml) was added, and the mixture extracted with diethyl ether (2 × 40 ml), dried ($MgSO_4$), and the solvents removed *in vacuo*. Short path distillation (bp 68 °C, 0.2 mmHg) gave the oxime **9** (980 mg, 68%) as a pale yellow oil. $\nu_{max}$(film)/$cm^{-1}$ 2983 (s), 1879 (w); $\delta_H$ (400 MHz, $CDCl_3$) 1.41 (3H, d, *J* 6.4, C$H_3$), 4.80 (1H, app quintet t, *J* 6.4, 1.1, $CH_3$C*H*), 5.19 (1H, app dt, *J* 10.6, 1.3, CH=C*H*H), 5.30 (1H, app dt, *J* 17.3, 1.4, CH=CH*H*), 5.99 (1H, ddd, *J* 17.3, 10.7, 6.2, C*H*=$CH_2$), 7.35–7.41 (3H, m, aromatic C*H*), 7.57–7.61 (2H, m, aromatic C*H*), 8.11 (1H, s, C*H*=N); $\delta_C$ (50 MHz, $CDCl_3$) 19.8 (*C*$H_3$), 80.1 ($CH_3$*C*H), 115.8 (CH=*C*$H_2$), 127.1, 128.7, 129.7 (aromatic *C*H), 132.6 (*ipso*-*C*), 139.5 (*C*H=$CH_2$), 148.5 (*C*H=N); *m*/*z* (APCI) 176 ($MH^+$, 10%), 122 (PhCHNO$H_2^+$, 100%); HRMS calculated for $C_{11}H_{14}NO^+$: 176.1075. Found: 176.1072.

### Benzaldehyde *O*-(1-methylbut-2-enyl)oxime 10

Phosphorus tribromide (0.53 ml, 5.6 mmol) was added in a dropwise manner to a solution of (*E*)-pent-3-en-2-ol (1.53 ml, 15 mmol) in diethyl ether (50 ml), cooled to 0 °C. The mixture was stirred for 24 h, and then used in the next step without purification. Benzaldehyde oxime (2.43 g, 20 mmol) and potassium *tert*-butoxide were dissolved in THF (50 ml) at 0 °C. After 30 min, the solution of bromide was transferred to the mixture by cannula, and the resulting mixture heated to reflux for 18 h. After cooling, water (50 ml) was added, the mixture extracted with diethyl ether (3 × 50 ml), dried ($MgSO_4$), and the solvent removed *in vacuo*. Column chromatography (10% $Et_2O$–petrol (40–60), $SiO_2$) gave the oxime **10** (1.22 g, 43%) as a colourless oil (*E* : *Z* 83 : 17). Data for major (*E*)-isomer; $\nu_{max}$/$cm^{-1}$ (film) 2979 (s), 1890 (w), 1676 (m); $\delta_H$ (400 MHz, $CDCl_3$) 1.39 (3H, d, *J* 6.4, C$H_3$), 1.74 (3H, app d, *J* 6.7, C$H_3$), 4.75 (1H, app quintet, *J* 6.5, OC*H*), 5.58–5.66 (1H, m, C*H*=CH), 5.73–5.82 (1H, m, CH=C*H*), 7.32–7.40 (3H, m, aromatic C*H*), 7.57–7.60 (2H, m, aromatic C*H*), 8.09 (1H, s, C*H*=N); $\delta_C$ (50 MHz, $CDCl_3$) 17.9 (*C*$H_3$), 20.1 (*C*$H_3$), 79.9 ($CH_3$*C*HCH=CH), 127.0, 127.7, 128.6, 129.5, 132.3 (*C*H=CH, CH=*C*H and Ar*C*H), 132.7 (*ipso*-*C*), 148.1 (*C*H=N); *m*/*z* (APCI) 190 ($MH^+$, 15%), 122 (PhCHNO$H_2^+$, 100%), 106 (10%); HRMS calculated for $C_{12}H_{16}NO^+$: 190.1232. Found: 190.1228.

**Acetophenone *O*-allyloxime 11**[10]

From acetophenone oxime (1.00 g, 7.40 mmol) and allyl bromide (0.98 g, 8.14 mmol), the oxime **11** (1.21 g, 93%) was obtained as a colourless oil after short path distillation (bp 95 °C, 4 mmHg; lit.,[31] 89 °C, 6 mmHg); $\delta_H$ (500 MHz, $CDCl_3$) 2.28 (3H, s, C$H_3$), 4.73 (2H, app dt, *J* 5.7, 1.4, OC$H_2$), 5.25 (1H, app dq, *J* 10.4, 1.3, CH=CH*H*), 5.36 (1H, app dq, *J* 17.3, 1.6, CH=CH*H*), 6.09 (1H, ddt, *J* 17.3, 10.4, 5.7, C*H*=$CH_2$), 7.35–7.41 (3H, m, aromatic C*H*), 7.53–7.68 (2H, m, aromatic C*H*).

**General procedure for the reduction of the oxime ethers**

*Method A*: pyridine–borane complex (3 eq.) was added to a stirred 0.5 M solution of the allylic oxime (1 eq.) in absolute ethanol at 0 °C, followed by the dropwise addition of a solution of 10% HCl in water (4 ml per mmol of oxime) over a period of five minutes. The mixture was warmed to room temperature and stirred for a further 1 h after which time the mixture was cooled to 0 °C, saturated aqueous sodium carbonate solution added until the acid was neutralised, and the mixture extracted with dichloromethane. The combined organic extracts were dried ($MgSO_4$), concentrated *in vacuo* and the resulting yellow oil purified by reduced pressure short path distillation to give the desired hydroxylamine.

*Method B*: pyridine–borane complex (3 eq.) was added to a stirred 0.5 M solution of the allylic oxime (1 eq.) in absolute ethanol at 0 °C, followed by the dropwise addition of a solution of 20% HCl in absolute ethanol (2 ml per mmol of oxime) over a period of five minutes. The mixture was warmed to room temperature and stirred for a further 24 h, then cooled and a saturated solution of sodium carbonate added until the acid was neutralised. The mixture was extracted with dichloromethane, the combined organic extracts dried ($MgSO_4$) and concentrated *in vacuo*, and the residue purified by short path distillation at reduced pressure or by column chromatography.

***N*-Benzyl-*O*-allylhydroxylamine 12**[21]

From oxime **5** (2.0 g, 12.4 mmol) and pyridine–borane complex (3.5 g, 37.2 mmol) using method A, **12** (1.90 g, 94%) was obtained as a colourless oil after short path distillation (bp 110 °C, 4 mmHg); $\nu_{max}$/$cm^{-1}$ (film) 3260, 1645, 1454, 1421; $\delta_H$ (500 MHz, $CDCl_3$) 4.08 (2H, s, PhC$H_2$), 4.18 (2H, app dt, *J* 5.9, 1.3, OC$H_2$), 5.18 (1H, app dq, *J* 10.4, 1.3, CH=CH*H*), 5.26 (1H, app dq, *J* 17.3, 1.6, CH=CH*H*), 5.70 (1H, br s, N*H*), 5.91 (1H, ddt, *J* 17.3, 10.4 and 5.9, C*H*=$CH_2$), 7.28–7.38 (5H, m, aromatic C*H*); $\delta_C$ (50 MHz, $CDCl_3$) 56.2 (Ph*C*$H_2$), 74.8 (O*C*$H_2$), 117.3 (CH=*C*$H_2$), 127.3, 128.2, 128.8 (aromatic *C*H), 134.6 (*C*H=$CH_2$), 137.6 (Ar*C*); *m*/*z* (APCI) 164 ($MH^+$, 100%), 108 ($PhCH_2NH_3^+$, 11%), 106 ($PhCHNH_2^+$, 22%); calculated for $C_{10}H_{13}NO$: C 73.6, H 8.0, N 8.6%. Found: C 73.9, H 8.1, N 9.0%.

***N*-Benzyl-*O*-(but-2-enyl)hydroxylamine 13**

From oxime **6** (1.83 g, 10.4 mmol) and pyridine–borane complex (2.92 g, 31.2 mmol) using method A, **13** (1.56 g, 85%) was obtained as a colourless oil (*E* : *Z* 76 : 24) by short path distillation (bp 112 °C, 4 mmHg); $\nu_{max}$/$cm^{-1}$ (film) 3259 (m), 2915 (s), 1950 (w), 1877 (w), 1808 (w), 1673 (m), 1604 (m); $\delta_H$ (400 MHz, $CDCl_3$) 1.64 (3H, ddt, *J* 6.8, 1.7, 0.8, (*Z*)-C$H_3$), 1.71 (3H, app dq, *J* 6.4, 1.3, (*E*)-C$H_3$), 4.07 (2H, s, (*E*)-PhC$H_2$), 4.08 (2H, s, (*Z*)-PhC$H_2$), 4.10 (2H, app dquintet, *J* 6.5, 1.1, (*E*)-OC$H_2$), 4.24 (2H, m, (*Z*)-OC$H_2$), 5.52–5.56 (1H, m, (*E*)- and (*Z*)-C*H*=CHCH$_3$), 5.56–5.76 (2H, m, (*E*)- and (*Z*)-CH=C*H*CH$_3$ and N*H*), 7.26–7.39 (5H, m, aromatic C*H*); $\delta_C$ (125 MHz, $CDCl_3$) 13.1 ((*Z*)-*C*H$_3$), 17.8 ((*E*)-*C*H$_3$), 56.4 (N*C*$H_2$), 69.1 ((*Z*)-O*C*$H_2$), 74.6 ((*E*)-O*C*$H_2$), 126.0, 126.8, 127.0, 127.3, 128.3, 128.5, 128.9, 130.3 (aromatic *C*H and *C*H=*C*H), 137.5 (*ipso*-*C*); *m*/*z* (APCI) 178 ($MH^+$, 40%), 124 ($PhCH_2NHOH_2^+$, 20%), 107 (100%), 106 ($MH^+$ − $CH_3CH$=$CHCH_2OH$, 70%); HRMS calculated for $C_{11}H_{16}NO^+$: 178.1232; Found: 178.1232.

***N*-Benzyl-*O*-(3-methylbut-2-enyl)hydroxylamine 14**

From oxime **7** (2.50 g, 13.2 mmol) and pyridine–borane complex (3.69 g, 39.7 mmol) using method A, **14** (2.02 g, 80%) was obtained as a colourless oil by column chromatography (25% $Et_2O$–petrol (40–60), $SiO_2$). $\nu_{max}$/$cm^{-1}$ (film) 3258 (m), 2914 (s), 1949 (w), 1876 (w), 1809 (w), 1674 (s), 1604 (w); $\delta_H$ (200 MHz, $CDCl_3$) 1.67 (3H, s, C$H_3$), 1.76 (3H, s, C$H_3$), 4.08 (2H, s, PhC$H_2$), 4.18 (2H, d, *J* 7.1, OC$H_2$), 5.35 (1H, tsept, *J* 7.1, 1.4, OCH$_2$C*H*), 5.72 (1H, br s, N*H*), 7.28–7.42 (5H, m, aromatic C*H*); $\delta_C$ (50 MHz, $CDCl_3$) 17.9 (*C*H$_3$), 25.7 (*C*H$_3$), 56.5 (Ph*C*$H_2$), 70.5 (*C*$H_2$O), 120.4 (*C*H=C(CH$_3$)$_2$), 127.6, 128.6, 129.2 (aromatic *C*H), 138.0, 138.2 (*ipso*-*C* and CH=*C*(CH$_3$)$_2$); *m*/*z* (APCI) 192 ($MH^+$, 60%), 179 (55%), 136 (25%), 124 (80%), 108 (100%), 106 (80%); HRMS calculated for $C_{12}H_{18}NO^+$: 192.1388. Found: 192.1380.

**(*E*)-*N*-Benzyl-*O*-(3-phenylallyl)hydroxylamine 15**

From oxime **8** (3.9 g, 16.5 mmol) and pyridine–borane complex (4.7 g, 50.5 mmol) using method B, **15** (3.32 g, 84%) was obtained as a colourless oil by column chromatography (33% $Et_2O$–petrol (40–60), $SiO_2$) which solidified on standing to give a cream solid (mp 35–36 °C). $\nu_{max}$/$cm^{-1}$ (film) 3260 (m), 3208 (s), 1950 (w), 1878 (w), 1807 (w), 1657 (w), 1599 (m), 1578 (m); $\delta_H$ (400 MHz, $CDCl_3$) 4.11 (2H, s, PhC$H_2$), 4.33 (2H, dd, *J* 6.4, 1.3, OC$H_2$), 5.78 (1H, s, N*H*), 6.27 (1H, dt, *J* 15.9, 6.4, CH=C*H*CH$_2$), 6.59 (1H, d, *J* 15.9, C*H*=CHCH$_2$), 7.23–7.40 (10H, m, aromatic C*H*); $\delta_C$ (50 MHz, $CDCl_3$) 56.7 (Ph*C*$H_2$), 74.8 (*C*$H_2$O), 125.7, 126.6, 127.5, 127.7, 128.5, 128.6, 129.1, 133.2 (*C*H=*C*H and aromatic *C*H), 136.8, 137.6 (*ipso*-*C*): *m*/*z* (APCI) 240 ($MH^+$, 5%), 133 (75%), 117 (30%), 105 (100%); calculated for $C_{16}H_{17}NO$: C 80.3, H 7.2, N 5.85. Found: C 80.1, H 7.0, N 5.65%.

***N*-Benzyl-*O*-(1-methyl-allyl)hydroxylamine 16**

From oxime **9** (878 mg, 5.02 mmol) and pyridine–borane complex (1.9 ml, 15 mmol) using method B, **16** (614 mg, 69%) was obtained as a colourless oil by column chromatography (30% $Et_2O$–petrol (40–60), $SiO_2$); $\nu_{max}$/$cm^{-1}$ (film) 3259 (m), 2980 (s), 1950 (w), 1871 (w), 1811 (w), 1642 (w), 1604 (w); $\delta_H$ (400 MHz, $CDCl_3$) 1.20 (3H, d, *J* 6.7, C$H_3$), 4.11 (2H, s, PhC$H_2$), 4.14 (1H, m, CH$_3$C*H*), 5.12 (1H, d, *J* 10.4, CH=CH*H*), 5.20 (1H, app dt, *J* 17.3, 1.3, CH=CH*H*), 5.54 (1H, br s, N*H*), 5.81 (1H, ddd, *J* 17.3, 10.4, 6.7, C*H*=$CH_2$), 7.26–7.37 (5H, m, aromatic C*H*); $\delta_C$ (50 MHz, $CDCl_3$) 19.4 (*C*H$_3$), 56.8 (Ph*C*$H_2$), 79.7 (*C*HCH$_3$), 115.9 (CH=*C*$H_2$), 127.6, 128.6, 129.4 (aromatic *C*H), 137.9 (*ipso*-*C*), 140.4 (*C*H=$CH_2$); *m*/*z* (APCI) 178 ($MH^+$, 100%), 124 ($PhCH_2NH_2OH^+$, 15%), 107 (15%); HRMS calculated for $C_{11}H_{16}NO^+$: 178.1232. Found: 178.1229.

***N*-Benzyl-*O*-(1-methylbut-2-enyl)hydroxylamine 17**

From oxime **10** (432 mg, 2.29 mmol) and pyridine–borane complex (0.86 ml, 6.86 mmol) using method B, **17** (356 mg, 82%) was obtained as a colourless oil (*E* : *Z* 83 : 17) by column chromatography (10% $Et_2O$–petrol (40–60), $SiO_2$); $\nu_{max}$/$cm^{-1}$ (film) 3258 (m), 2973 (s), 1948 (w), 1878 (w), 1808 (w), 1674 (m), 1604 (m); $\delta_H$ (400 MHz, $CDCl_3$) 1.16 (3H, d, *J* 6.4, (*Z*)-OCHC$H_3$), 1.18 (3H, d, *J* 6.5, (*E*)-OCHC$H_3$), 1.65 (3H, dd, *J* 6.9, 1.8, (*Z*)-CH=CHC$H_3$), 1.69 (3H, ddd, *J* 6.4, 1.5, 0.6, (*E*)-CH=CHC$H_3$), 4.04 (2H, s, (*E*)-PhC$H_2$), 4.05 (2H, s, (*Z*)-PhC$H_2$), 4.09 (1H, m, (*E*)-OC*H*CH$_3$), 4.52 (1H, dqd, *J* 8.7, 6.4, 1.1, (*Z*)-OC*H*CH$_3$), 5.35 (1H, ddq, *J* 11.0, 8.7, 1.8, (*Z*)-C*H*=CHCH$_3$), 5.41 (1H, ddq, *J* 15.4, 7.4, 1.5, (*E*)-C*H*=CHCH$_3$), 5.48 (1H, br s, N*H*), 5.58 (1H, dqd, *J* 11.0, 6.9, 1.1, (*Z*)-CH=

C*H*$CH_3$), 5.65 (1H, dqd, *J* 15.4, 6.4, 0.9, (*E*)-CH=C*H*$CH_3$), 7.28–7.37 (5H, m, aromatic C*H*); $\delta_C$ (50 MHz, $CDCl_3$) 17.8 (*C*$H_3$), 19.8 (*C*$H_3$), 56.7 (Ph*C*$H_2$), 79.1 ($CH_3$*C*H), 127.3, 127.4, 128.3, 129.1, 133.0 (*C*H=*C*H and aromatic *C*H), 137.7 (*ipso-C*); *m*/*z* (APCI) 192 ($MH^+$, 10%), 179 (40%), 124 ($PhCH_2NH_2OH^+$, 100%); HRMS calculated for $C_{12}H_{18}NO^+$: 192.1388. Found: 192.1396.

### *N*-(1-Phenylethyl)-*O*-allylhydroxylamine 18[10]

From allyl oxime **11** (1.21 g, 6.91 mmol) and pyridine–borane complex (2.40 g, 20.7 mmol) using method B, **18** (1.02 g, 83%) was obtained as a colourless oil by short path distillation (bp 104 °C, 4 mmHg). $\delta_H$ (500 MHz, $CDCl_3$) 1.39 (3H, d, *J* 6.7, C*H*$_3$), 4.11 (1H, dd, *J* 12.6, 5.9, OC*H*H), 4.17 (1H, dd, *J* 12.6, 5.9, OCH*H*), 4.17 (1H, q, *J* 6.7, $CH_3$C*H*), 5.16 (1H, app d, *J* 10.4, CH=C*H*H), 5.23 (1H, app dq, *J* 17.3, 1.5, CH=CH*H*), 5.61 (1H, br s, N*H*), 5.88 (1H, ddt, *J* 17.3, 10.4, 5.9, C*H*=$CH_2$), 7.26–7.38 (5H, m, aromatic C*H*).

### General procedure for the rearrangement reaction

*n*-Butyllithium (1.1–1.3 eq.) was added to a 0.1 M solution of hydroxylamine (1 eq.) in anhydrous THF at −78 °C under nitrogen. After stirring for 1 h the reaction was allowed to warm to room temperature and was stirred for a further 30 min. The reaction was quenched with distilled water, extracted with diethyl ether, the combined organic extracts dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by column chromatography on deactivated silica gel (1% $Et_3N$ in petrol) to give the desired hydroxylamine rearrangement product.

### *N*-Benzyl-*N*-(1-phenylallyl)hydroxylamine 19[33]

Addition of *n*-butyllithium (1.66 M, 1.26 ml, 2.09 mmol) and the hydroxylamine **15** (500 mg, 2.09 mmol) gave the hydroxylamine **19** (201 mg, 40%) as a cream solid (mp 91–92 °C) after chromatography (10% $Et_2O$–petrol (40–60), $SiO_2$). $\nu_{max}$/$cm^{-1}$ (KBr disc) 3213 (m), 2866 (s); $\delta_H$ (400 MHz, $CDCl_3$) 3.77 (1H, d, *J* 13.6, PhC*H*H), 3.91 (1H, br d, PhCH*H*), 4.31 (1H, d, *J* 8.5, NC*H*Ph), 4.65 (1H, br s, O*H*), 5.25 (1H, dd, *J* 10.0, 1.3, CH=C*H*H), 5.31 (1H, d, *J* 17.3, CH=CH*H*), 6.18 (1H, ddd, *J* 17.3, 10.0, 8.5), 7.21–7.53 (10H, m, aromatic C*H*); $\delta_C$ (100 MHz, $CDCl_3$) 61.1 (Ph*C*$H_2$), 75.3 (Ph*C*H), 117.9 (CH=*C*$H_2$), 127.3, 127.5, 128.2, 128.3, 128.7, 129.6 (aromatic *C*H), 137.7 (*C*H=$CH_2$), 138.0, 141.0 (*ipso-C*); *m*/*z* (CI) 240 ($MH^+$, 100%), 224 (32%), 222 ($MH^+ - H_2O$, 27%), 117 (PhCHCH=$CH_2^+$, 45%); HRMS calculated for $C_{16}H_{17}NO^+$: 240.1388. Found: 240.1383.

### *N*-Benzyl-*N*-allylhydroxylamine 22[32]

Addition of *n*-butyllithium (1.66 M, 0.96 ml, 1.60 mmol) to the hydroxylamine **12** (200 mg, 1.23 mmol) gave the hydroxylamine **22** (122 mg, 61%) as a yellow oil after chromatography (10% $Et_2O$–petrol (40–60), $SiO_2$); $\nu_{max}$/$cm^{-1}$ (film) 3217, 1644, 1494, 1453; $\delta_H$ (500 MHz, $CDCl_3$) 3.36 (2H, d, *J* 6.5, NC$H_2$CH=), 3.79 (2H, s, NC$H_2$Ph), 5.20 (1H, app d, *J* 10.3, CH=C*H*H), 5.24 (1H, app dq, *J* 17.2, 1.4, CH=CH*H*), 5.95 (1H, ddt, *J* 17.2, 10.3, 6.5, C*H*=$CH_2$), 7.27–7.35 (5H, m, aromatic C*H*); $\delta_C$ (125 MHz, $CDCl_3$) 62.4, 63.7 (N*C*$H_2$Ph and N*C*$H_2$CH=), 118.7 (CH=*C*$H_2$), 127.4, 128.2, 129.9 (aromatic *C*H), 133.7 (*C*H=$CH_2$), 136.9 (*ipso-C*); *m*/*z* (APCI) 164 ($MH^+$, 100%), 148 (7%); HRMS calculated for $C_{10}H_{14}NO^+$: 164.1075. Found: 164.1067.

### *N*-Benzyl-*N*-(1-methylallyl)hydroxylamine 23

Addition of *n*-butyllithium (2.59 M, 0.48 ml, 1.24 mmol) to the hydroxylamine **13** (200 mg, 1.13 mmol) gave the hydroxylamine **23** (118 mg, 59%) as a yellow oil after chromatography (10% $Et_2O$–petrol (40–60), $SiO_2$). $\nu_{max}$/$cm^{-1}$ (film) 3236, 1639, 1496, 1454; $\delta_H$ (500 MHz, $CDCl_3$) 1.26 (3H, d, *J* 6.6, C*H*$_3$), 3.33 (1H, app quintet, *J* 6.9, C*H*$CH_3$), 3.69 (1H, d, *J* 13.3, PhC*H*H), 3.87 (1H, d, *J* 13.3, PhCH*H*), 5.18 (1H, d, *J* 17.5, CH=C*H*H), 5.20 (1H, d, *J* 10.4, CH=CH*H*), 5.45 (1H, br s, O*H*), 5.97 (1H, ddd, *J* 17.5, 10.4, 7.5, C*H*=$CH_2$), 7.25–7.44 (5H, m, aromatic C*H*); $\delta_C$ (125 MHz, $CDCl_3$) 17.5 (*C*$H_3$), 60.7 (Ph*C*$H_2$), 64.6 (*C*H$CH_3$), 116.8 (CH=*C*$H_2$), 127.2, 128.2, 129.7 (aromatic *C*H), 137.9 (*ipso-C*), 138.4 (*C*H=$CH_2$); *m*/*z* (APCI) 178 ($MH^+$, 100%), 176 (10%), 162 ($C_{11}H_{16}N^+$, 31%), 160 ($C_{11}H_{14}N^+$, 29%), 124 ($PhCH_2NH_2OH^+$, 58%), 122 ($PhCH_2NOH^+$, 8%), 106 ($PhCHNH_2^+$, 46%); HRMS calculated for $C_{11}H_{16}NO^+$: 178.1232. Found: 178.1233.

### *N*-Benzyl-*N*-(1,1-dimethylallyl)hydroxylamine 24

Addition of *n*-butyllithium (1.66 M, 0.79 ml, 1.31 mmol) to the hydroxylamine **14** (250 mg, 1.31 mmol) gave, after stirring at −78 °C for 1 h, then heating at reflux for 2 h, the hydroxylamine **24** (119 mg, 60%) as a yellow oil after chromatography (10% $Et_2O$–petrol (40–60), $SiO_2$). $\nu_{max}$/$cm^{-1}$ (film) 3536 (s), 3442 (br, m), 1640 (m), 1606 (m); $\delta_H$ (200 MHz, $CDCl_3$) 1.31 (6H, s, C(C*H*$_3$)$_2$), 3.75 (2H, s, PhC$H_2$), 4.81 (1H, s, O*H*), 5.17 (1H, d, *J* 10.8, CH=C*H*H), 5.21 (1H, d, *J* 17.8, CH=CH*H*), 5.97 (1H, dd, *J* 17.8, 10.8, C*H*=$CH_2$), 7.26–7.35 (5H, m, aromatic C*H*); $\delta_C$ (50 MHz, $CDCl_3$) 22.8 (C(*C*$H_3$)$_2$), 57.1 (Ph*C*$H_2$), 63.1 (*C*(C$H_3$)$_2$), 113.6 (CH=C$H_2$), 127.1, 128.5, 129.5 (aromatic *C*H), 139.9 (*ipso-C*), 144.1 (*C*H=$CH_2$); *m*/*z* (APCI) 192 ($MH^+$, 15%), 159 (40%), 124 (100%); HRMS calculated for $C_{12}H_{18}NO^+$: 192.1388. Found: 192.1380.

### (*E*)-*N*-Benzyl-*N*-(but-2-enyl)hydroxylamine 25

Addition of *n*-butyllithium (2.5 M, 0.52 ml, 1.31 mmol) and the hydroxylamine **16** (211 mg, 1.19 mmol) gave the hydroxylamine **25** (115 mg, 55%) as a colourless oil after chromatography (10% $Et_2O$–petrol (40–60), $SiO_2$); $\nu_{max}$/$cm^{-1}$ (film) 3222 (s), 2917 (s), 1949 (w), 1878 (w), 1809 (w), 1671 (w), 1604 (w); $\delta_H$ (400 MHz, $CDCl_3$) 1.72 (3H, d, *J* 5.9, C*H*$_3$), 3.33 (2H, d, *J* 6.2, NC$H_2$CH), 3.78 (2H, s, NC$H_2$Ph), 5.57–5.65 (2H, m, $CH_2$C*H*=CH and O*H*), 5.70 (1H, dq, *J* 15.4, 5.9, $CH_2$CH=C*H*), 7.24–7.36 (5H, m, aromatic C*H*); $\delta_C$ (50 MHz, $CDCl_3$) 17.8 (*C*$H_3$), 61.4, 63.4 (Ph*C*$H_2$ and *C*$H_2$CH=CH), 126.4, 127.5, 128.4, 130.2, 130.4 (*C*H=*C*H and aromatic *C*H), 137.2 (*ipso-C*); *m*/*z* (APCI) 178 ($MH^+$, 100%), 160 ($MH^+ - H_2O$, 15%), 147 (30%), 124 ($PhCH_2NH_2OH^+$, 55%), 106 ($PhCH=NH_2^+$, 35%); HRMS calculated for $C_{12}H_{18}NO^+$: 178.1232. Found: 178.1232.

### *N*-Benzyl-*N*-(1-methylbut-2-enyl)hydroxylamine 26

Addition of *n*-butyllithium (2.5 M, 0.76 ml, 1.90 mmol) to the hydroxylamine **17** (330 mg, 1.73 mmol) gave the hydroxylamine **26** (183 mg, 55%) as a colourless oil after chromatography (10% $Et_2O$–petrol (40–60), $SiO_2$). $\nu_{max}$/$cm^{-1}$ (film) 3234 (br s), 2974 (s), 1948 (w), 1876 (w), 1809 (w), 1752 (w), 1667 (m), 1605 (m); $\delta_H$ (400 MHz, $CDCl_3$) 1.24 (3H, d, *J* 6.5, NCHC*H*$_3$), 1.74 (3H, d, *J* 4.9, CH=CHC*H*$_3$), 3.28 (1H, app quintet, *J* 6.6, NC*H*$CH_3$), 3.65 (1H, d, *J* 13.2, NC*H*H), 3.87 (1H, d, *J* 13.2, NCH*H*), 5.32–5.51 (1H, br s, O*H*), 5.53–5.66 (2H, m, C*H*=C*H*), 7.23–7.36 (5H, m, aromatic C*H*); $\delta_C$ (50 MHz, $CDCl_3$) 18.0 and 18.1 (*C*$H_3$), 60.6 (Ph*C*$H_2$), 63.8 ($CH_3$*C*H), 127.1, 128.0, 128.2, 129.7, 131.1 (*C*H=*C*H and aromatic *C*H), 138.0 (*ipso-C*); *m*/*z* (APCI) 192 ($MH^+$, 20%), 124 ($PhCH_2NHOH_2^+$, 100%); HRMS calculated for $C_{12}H_{18}NO^+$: 192.1388. Found: 192.1389.

### *N*-(1-Phenylethyl)-*N*-allylhydroxylamine 27[10]

Addition of *n*-butyllithium (2.10 M, 0.60 ml, 1.24 mmol) to the hydroxylamine **18** (200 mg, 1.13 mmol) gave the hydroxylamine **27** (105 mg, 53%) as a yellow oil after chromatography (10% $Et_2O$–petrol (40–60), $SiO_2$); $\delta_H$ (500 MHz, $CDCl_3$) 1.49 (3H, d, *J* 6.6, C*H*$_3$), 3.25–3.31 (2H, m, NC$H_2$), 3.83 (1H, q, *J* 6.6,

$CH_3CH$), 5.18 (1H, d, $J$ 10.9, CH=CH*H*), 5.18 (1H, d, $J$ 17.3, CH=CH*H*), 5.98 (1H, m, C*H*=$CH_2$), 7.26–7.40 (5H, m, aromatic C*H*).

**General procedure for the reduction of the hydroxylamines**

Hydroxylamine (1 eq.) was dissolved in 2 M HCl (10 ml) and zinc powder added (5 eq.) cautiously. The reaction was then heated at 80 °C for 1 h, cooled and neutralised with 2 M NaOH. The white suspension obtained was extracted with $Et_2O$ and dried ($MgSO_4$). Evaporation afforded the allylic amine that was determined to be >95% pure from the $^1$H NMR spectrum.

***N*-Benzyl-*N*-allylamine 28** [34]

From hydroxylamine **22** (100 mg, 0.61 mmol) and zinc powder (200 mg, 3.1 mmol), the desired amine **28** (81 mg, 90%) was obtained as a colourless oil. $\delta_H$ (200 MHz, $CDCl_3$) 3.29 (2H, dt, $J$ 6.0, 1.4, $CH_2$CH=$CH_2$), 3.80 (2H, s, PhC$H_2$), 5.10–5.26 (2H, m, CH=C$H_2$), 5.95 (1H, ddt, $J$ 17.2, 10.3, 6.0, C*H*=$CH_2$), 7.21–7.36 (5H, m, aromatic C*H*).

***N*-Benzyl-*N*-(1-methylallyl)amine 29** [35]

From hydroxylamine **23** (100 mg, 0.564 mmol) and zinc powder (183 mg, 2.82 mmol), the desired amine **29** (85 mg, 94%) was obtained as an oil. $\nu_{max}$/cm$^{-1}$ (film) 3318 (w), 2962 (s), 1640 (w), 1605 (w); $\delta_H$ (500 MHz, $CDCl_3$) 1.20 (3H, d, $J$ 6.5, C$H_3$), 1.52, (1H, br s, N*H*), 3.24 (1H, app quintet, $J$ 6.8, $CH_3$C*H*), 3.70 (1H, d, $J$ 13.1, PhC*H*H), 3.82 (1H, d, $J$ 13.1, PhCH*H*), 5.10 (1H, dd, $J$ 10.2, 1.5, CH=C*H*H), 5.15 (1H, app d, $J$ 17.2, CH=CH*H*), 5.74 (1H, ddd, $J$ 17.2, 10.2, 7.7, C*H*=$CH_2$), 7.23–7.36 (5H, m, aromatic C*H*); $\delta_C$ (125 MHz, $CDCl_3$) 21.7 (*C*$H_3$), 51.3 (Ph*C*$H_2$), 56.0 (*C*HCH$_3$), 114.7 (CH=*C*$H_2$), 126.8, 128.1, 128.4 (aromatic *C*H), 140.5 (*ipso-C*), 142.4 (*C*H=$CH_2$); *m*/*z* (APCI) 162 ($MH^+$, 100%), 108 (5%); calculated for $C_{11}H_{16}N^+$: 162.1283. Found: 162.1284.

***N*-Benzyl-*N*-(1,1-dimethylallyl)amine 30** [36]

From hydroxylamine **24** (51 mg, 0.27 mmol) and zinc powder (88 mg, 1.36 mmol), the desired amine **30** (43 mg, 92%) was obtained as an oil. $\delta_H$ (200 MHz, $CDCl_3$) 1.25 (6H, s, C(C$H_3$)$_2$), 3.65 (2H, s, PhC$H_2$), 5.08–5.16 (2H, m, CH=C$H_2$), 5.86 (1H, dd, $J$ 17.8, 10.4, C*H*=$CH_2$), 7.23–7.34 (5H, m, aromatic C*H*); $\delta_C$ (50 MHz, $CDCl_3$) 26.8 (2 × *C*$H_3$), 47.5 (Ph*C*$H_2$), 54.7 (*C*(CH$_3$)$_2$), 112.5 (CH=*C*$H_2$), 127.0, 128.4, 128.5 (aromatic *C*H), 141.3 (*ipso-C*), 146.2 (*C*H=$CH_2$).

***N*-Benzyl-*N*-(1-phenylallyl)amine 31** [37]

From hydroxylamine **19** (100 mg, 0.42 mmol) and zinc powder (140 mg, 2.1 mmol), the desired amine **31** (85 mg, 91%) was obtained as a yellow oil. $\delta_H$ (400 MHz, $CDCl_3$) 1.69 (1H, s, N*H*), 3.73 (1H, d, $J$ 13.3, PhC*H*H), 3.76 (1H, d, $J$ 13.3, PhCH*H*), 4.24 (1H, d, $J$ 7.1, C*H*CH=$CH_2$), 5.14 (1H, d, $J$ 10.1, CH=C*H*H), 5.24 (1H, d, $J$ 17.1, CH=CH*H*), 5.97 (1H, ddd, $J$ 17.1, 10.1, 7.1, C*H*=$CH_2$), 7.24–7.54 (10H, m, aromatic C*H*).

**(*E*)-*N*-Benzyl-*N*-(but-2-enyl)amine 32** [38]

From hydroxylamine **25** (109 mg, 0.615 mmol) and zinc powder (201 mg, 3.08 mmol), the desired amine **32** (69 mg, 70%) was obtained as a pale yellow oil. $\delta_H$ (400 MHz, $CDCl_3$) 1.70 (3H, d, $J$ 5.6, C$H_3$), 3.22 (2H, d, $J$ 5.4, $CH_2$CH=CH), 3.79 (2H, s, PhC$H_2$), 5.55–5.66 (2H, m, C*H*=C*H*), 7.25–7.33 (5H, m, aromatic C*H*); $\delta_C$ (125 MHz, $CDCl_3$) 17.7 (*C*$H_3$), 51.0, 53.1 (*C*$H_2$N*C*$H_2$), 126.8, 127.4, 128.1, 128.3, 129.2 (aromatic and alkene *C*H), 140.2 (*ipso-C*).

***N*-Benzyl-*N*-(1-methylbut-2-enyl)amine 33** [39]

From hydroxylamine **26** (181 mg, 0.948 mmol) and zinc powder (310 mg, 4.74 mmol), the desired amine **33** (137 mg, 83%) was obtained as a pale yellow oil. $\nu_{max}$/cm$^{-1}$ (film) 3168 (br m), 2971 (s), 1947 (w), 1874 (w), 1808 (w), 1668 (w), 1604 (m); $\delta_H$ (400 MHz, $CDCl_3$) 1.16 (3H, d, $J$ 6.6, NCHC$H_3$), 1.71 (3H, dd, $J$ 6.4, 1.6, CH=CHC$H_3$), 3.18 (1H, app quintet, $J$ 6.9, NC*H*CH$_3$), 3.68 (1H, d, $J$ 13.1, PhC*H*H), 3.79 (1H, d, $J$ 13.1, PhCH*H*), 5.35 (1H, ddq, $J$ 15.2, 7.9, 1.6, C*H*=CHCH$_3$), 5.55 (1H, dqd, $J$ 15.2, 6.4, 0.7, CH=C*H*CH$_3$), 7.22–7.37 (5H, m, aromatic C*H*); $\delta_C$ (100 MHz, $CDCl_3$) 17.7 (CH=CH*C*H$_3$), 22.0 (NCH*C*H$_3$), 51.3 (N*C*H$_2$), 55.2 (N*C*HCH$_3$), 125.8 (*C*H=CH), 126.8, 128.2, 128.4 (aromatic *C*H), 135.4 (CH=*C*H), 140.7 (*ipso-C*); *m*/*z* (APCI) 175 ($MH^+$, 5%), 163 (10%), 124 (20%), 108 ($PhCH_2NH_2^+$, 100%); calculated for $C_{12}H_{18}N^+$: 176.1439. Found: 176.1438.

***N*-(1-Phenylethyl)-*N*-allylamine 34** [40]

From hydroxylamine **27** (100 mg, 0.56 mmol) and zinc powder (183 mg, 2.8 mmol), the desired amine **34** (85 mg, 94%) was obtained as a colourless oil. $\delta_H$ (200 MHz, $CDCl_3$) 1.39 (3H, d, $J$ 6.6, C$H_3$), 1.92 (1H, br s, N*H*), 3.11 (2H, d, $J$ 6.0, NC$H_2$), 3.82 (1H, q, $J$ 6.6, C*H*CH$_3$), 5.08 (1H, ddt, $J$ 10.2, 1.9, 1.3, CH=C*H*H), 5.14 (1H, app dq, $J$ 17.2, 1.6, CH=CH*H*), 5.91 (1H, ddt, $J$ 17.2, 10.2, 6.0, C*H*=$CH_2$), 7.22–7.40 (5H, m, aromatic C*H*).

## Acknowledgements

The authors wish to acknowledge the support of the EPSRC for a studentship and the SCI for a Messel scholarship (T. G. R. S.) and New College, Oxford for a Junior Research Fellowship (A. D. S.) and Fundação para a Ciência e a Tecnologia (Programa Praxis XXI) for funding (F. C. T.).

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