Synthesis and Radical Reactions of Isomeric Alkenyl Oxaziridines

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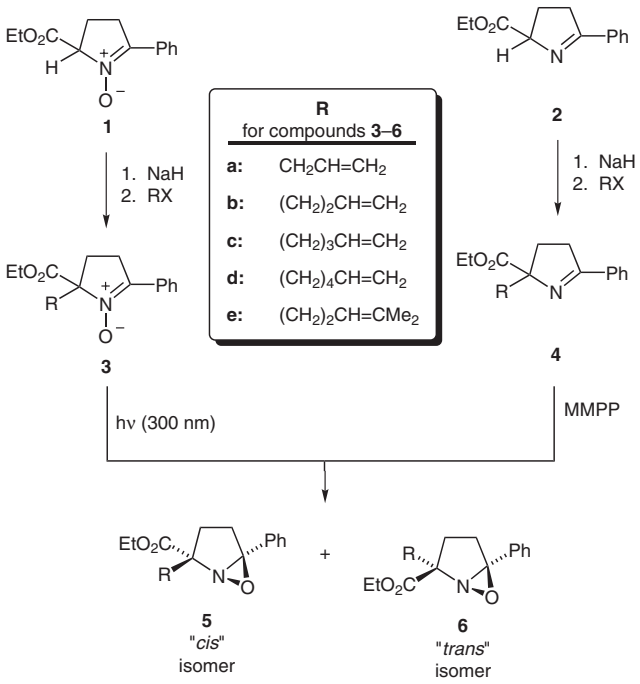
The authors wish to dedicate this paper to Professor Glen Deacon on the occasion of his 70th birthday.

Abstract: Several alkenyl oxaziridines were prepared either by photoisomerisation of the precursor nitrones, or by peracid oxidation of the analogous pyrrolines. In each case the oxaziridines were produced as separable mixtures of diastereoisomers, and reasons for the observed stereoselectivity are discussed. Reaction of the oxaziridines with iron(II) sulfate, tributyltin hydride, or copper(I)triphenylphosphine chloride tetramer gave products arising from deoxygenation in many cases; however the *trans*-isomers also gave products derived from cyclisation of the intermediate aminyl radicals onto the pendant alkenyl chains.

Key words: oxaziridines, radical reactions, nitrones, stereoselectivity, aminyl radicals

Alkaloids, especially those containing saturated nitrogen heterocycles, can possess remarkably varied structures and display significant and varied biological activity.[1,2] Potent examples of this class are found among the bicyclic structures such as pyrrolizidines,[3] indolizidines and quinolizidines,[4] where extreme toxicities have been observed. While many approaches have been adopted for the synthesis of these important skeletons,[5] aminyl radical chemistry[6] appears to have found relatively little application thus far in pyrrolizidine synthesis.[7] We have previously reported[8] our initial investigations on the use of oxaziridines as precursors for aminyl radicals, where reductive cleavage of the N–O bond and subsequent cyclisation onto a pendant alkenyl group provided a new route to the bicyclic core. We now wish to present full details of our studies on oxaziridine-derived aminyl radicals as a novel route to these fascinating structures.

The initial phase of the investigation focussed on development of a reliable synthesis of alkenyl oxaziridines; these useful intermediates have been employed by us previously in a new approach to tropane alkaloids.[9] Synthesis of the precursor oxaziridines was effected by two routes: peracid oxidation of imines,[10] or electrocyclic ring closure of imine *N*-oxides (nitrones).[11] Both synthetic strategies had similar initial stages: deprotonation of the known nitrone **1**[12] or the pyrroline **2**[12] with sodium hydride and subsequent treatment of the resonance-stabilised anions with the appropriate alkenyl halide gave good to excellent yields of the monoalkylated products **3** and **4** respectively (Scheme 1). While the reactions with alkenyl halides were



Scheme 1

routinely successful, it was disappointing that attempted alkylation with 4-iodobut-1-yne gave no identifiable products.

In all cases the alkenylation was entirely regioselective, with no evidence of the isomeric C-2 alkylated product in the ^{1}H NMR spectra of the crude products. Spectroscopic characterisation of the alkylated nitrones **3** and pyrrolines **4** showed many similarities; however, there were two noteworthy differences. In the ^{1}H NMR spectra of the pyrrolines **4**, the ethyl esters behaved as simple first-order systems where the OCH_2 was observed as a well-resolved quartet. In contrast, the corresponding NMR spectra of the nitrones **3** gave an extremely complex pattern for these two diastereotopic protons. The second key difference was noted in the ^{13}C NMR spectra: for the pyrrolines **4**, the imine carbon resonance was observed at a similar chemical shift to that of the ester carbon, whereas in the corresponding nitrones **3**, this resonance was shifted upfield by about 40 ppm.

Preparation of the desired oxaziridines was carried out by photoisomerisation of the nitrones **3** in benzene solution, and also by oxidation of methanolic solutions of the pyrrolines **4** with magnesium monoperphthalate (MMPP).

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Both modes of reaction produced mixtures of two isomeric oxaziridines **5** and **6** (Scheme 1) that could be separated by careful preparative thin layer chromatography; their identity could be deduced readily from analysis of the ^{1}H NMR spectra, as outlined below. In all cases the peracid oxidation favoured the *cis* structures **5** (where the alkenyl chain and the oxaziridine oxygen are on the same face; isolated as the less polar isomers i.e., those compounds with higher R_f), whereas the photocyclisation favoured the *trans* isomers **6** (the more polar isomers i.e., the compounds with lower R_f). Yields are given in Tables 1 and 2.

The NMR spectra of the isomeric oxaziridines were quite similar; however, three distinct differences were noted. In all cases, the less polar isomers (those with higher R_f) consistently displayed both the CH_3 and CH_2 resonances for the ethyl esters at lower chemical shift (upfield) in the ^{1}H NMR spectra compared with the more polar compounds. Also two multiplets were observed quite close together in the region δ = ca. 2.5–3.0 for the less polar isomers; these multiplets were well separated for the more polar (low R_f) isomers. These factors suggested that all of the high R_f isomers have similar stereochemistry, and all of the low R_f isomers likewise are structurally related.

In order to facilitate assignment of stereochemistry to each of the sets of isomers, a NOESY experiment was carried out on each of the butenyl isomers. The less polar isomer **5b** showed a weak but real and positive interaction between the ester methyl group and the aromatic *ortho* protons (Figure 1). No such interaction was observed for the more polar isomer **6b**. Therefore the less polar isomers **5** (with the ester signals at lower chemical shift, produced as major products by MMPP oxidation of the pyrrolines) are believed to be the stereoisomers where the Ph and ester groups are *cis*. This results in the alkenyl chain and the oxaziridine oxygen being *cis*. For the sake of convenience, these isomers are therefore designated as *cis* isomers. The more polar isomers, produced as major products by photoisomerisation of the nitrones, have the alkenyl sidechain and oxaziridine oxygen *trans*; in this study they are called the *trans* isomers. (While Cahn–Ingold–Prelog based nomenclature is formally more correct, assignment of priorities to the alkenyl chains sees the designations change: the *cis*-allyl compound **5a** is 2*R**,5*S**, while the other *cis* compounds **5b** to **5e** are 2*R**,5*R**.)

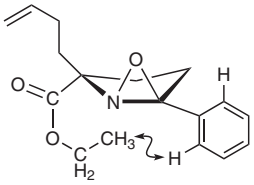


Figure 1 Key NOE interaction for **5b**

The observed deshielding of the ester group in the *trans* isomer (where the ester and the oxaziridine oxygen are on the same face) is consistent with the observations of Crotti and co-workers[13] where synthesis of *cis* and *trans* isomers of methyl 2,3-epoxycyclopentane-1-carboxylate and their ^{1}H NMR analysis showed that the methyl signal appeared further downfield when the epoxide oxygen and ester group were *cis*.

Table 1 Preparation of Oxaziridines from Photocyclisation of Nitrones **3**

Nitrone	Alkenyl chain	Total yield (%)	Yield of *cis* isomer **5** (%)	Yield of *trans* isomer **6** (%)	Ratio *cis*/*trans*
3a	$CH_2CH{=}CH_2$	67	19	48	1:2.5
3b	$(CH_2)_2CH{=}CH_2$	81	30	51	1:1.7
3c	$(CH_2)_3CH{=}CH_2$	81	36	45	1:1.3
3d	$(CH_2)_4CH{=}CH_2$	78	37	41	1:1.1
3e	$(CH_2)_2CH{=}CMe_2$	77	14	63	1:4.5

Table 2 Preparation of Oxaziridines from Peracid Oxidation of Pyrrolines **4**

Pyrroline	Alkenyl chain	Total yield (%)	Yield of *cis* isomer **5** (%)	Yield of *trans* isomer **6** (%)	Ratio *cis*/*trans*
4a	$CH_2CH{=}CH_2$	90	72	18	4.0:1
4b	$(CH_2)_2CH{=}CH_2$	91	72	19	3.8:1
4c	$(CH_2)_3CH{=}CH_2$	95	70	25	2.8:1
4d	$(CH_2)_4CH{=}CH_2$	89	62	27	2.3:1
4e	$(CH_2)_2CH{=}CMe_2$	97	66	31	2.1:1

While hydrogen-bond formation has been invoked as a directing influence for peracid oxidations by Crotti[13] in the epoxidation of methyl cyclopent-2-ene-1-carboxylate using *m*-chloroperbenzoic acid (MCPBA), it appears to have little, if any, effect as both Crotti,[13] and Koga,[14] have demonstrated that MCPBA epoxidation of this alkene gave (essentially) a 1:1 mixture of diastereoisomers. In our case, use of MMPP for epoxidation of the related pyrrolines **4** has produced a consistent (if sometimes small) excess of the *cis* diastereoisomer **5**. This is consistent with chelation of the magnesium ion between the imine nitrogen and ester carbonyl generating a ∪-shaped bicyclo[3.3.0]octane-like structure (Figure 2). Attack on the *endo* face would be disfavoured and hence the peracid preferentially attacks the imine from the less hindered *exo* face, *trans* to the ester group. It is noteworthy that the diastereoselectivity decreases as the size of the alkenyl group increases.

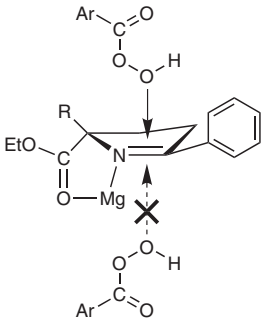


Figure 2 Possible formation of *cis*-oxaziridine by imine epoxidation

While MMPP oxidation of the pyrrolines **4** favours the *cis* isomers **5**, synthesis of the oxaziridines by photocyclisation of the nitrones **3** consistently produces a small excess of the *trans* diastereoisomer **6**. As the $2\pi + 2\sigma$ electrocyclic ring closure progresses, the transition state leading towards the *cis* isomer would bring the bulkier ester and phenyl groups closer together and, thus, formation of the *cis* isomer would have a somewhat higher energy of activation (see Figure 3). As a result, the *trans* isomer is formed preferentially. Again, as the size of the alkenyl group increases, the diastereoselectivity decreases; the higher preference for the *trans* isomer **6e** is intriguing.

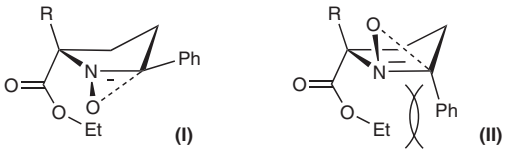
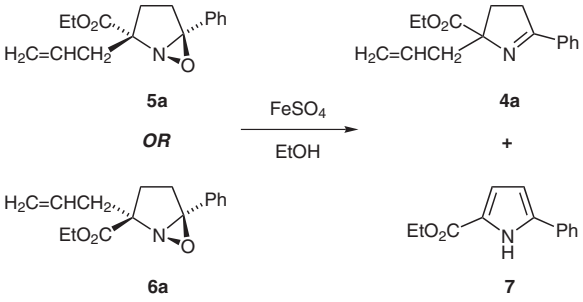


Figure 3 Possible transition structures leading to *trans* **I** and *cis* **II** oxaziridines

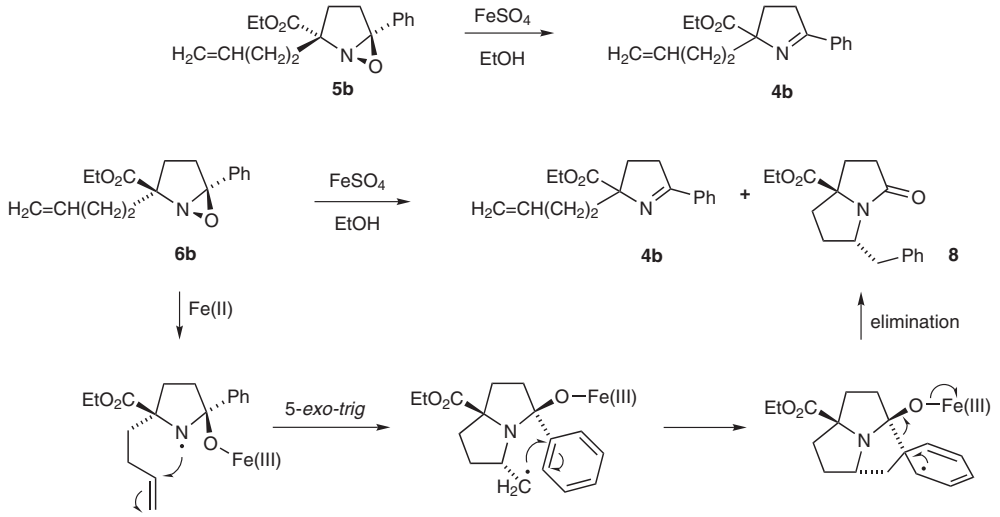
Generation of aminyl radicals from oxaziridines is achieved by reductive cleavage of the N–O bond;[15] this normally requires a transition metal such as iron(II). Initial studies focussed on reactions with iron(II) sulfate[16] in boiling ethanol and, as can be seen from Table 3, a major outcome in many cases was simple deoxygenation to give the pyrroline **4**. Iron(II)-promoted reaction of the allyl compounds **5a** and **6a** gave not only the pyrroline **4a** in ca. 40% yield, but also a significant amount of the pyrrole **7**[12] (ca. 30%) resulting from deoxygenation and accompanying loss of the pendant allyl group (Scheme 2).



Scheme 2

The facile loss of the allyl group is in stark contrast to the fact that no dealkylation is observed for any other oxaziridines in this study. Both isomeric allyl compounds behaved similarly, except that the reaction of the *trans* compound **6a** produced a small amount of unidentified cyclic materials in addition to the pyrroline **4a** and pyrrole **7**. Treatment of the isomeric oxaziridines **5a** and **6a** with Bu_3SnH and AIBN in boiling benzene gave poor yields of pyrroline **4a** along with unreacted starting material. A third approach saw the oxaziridines reduced using copper(I) triphenylphosphine chloride tetramer[17] in THF; this reaction protocol again saw deoxygenation as the major outcome, with substantially more pyrrole **7** being isolated in each case. In a similar manner to the iron(II) case, reaction of the *trans* isomer **6a** with $[Cu(PPh_3)Cl]_4$ also gave small amounts of unidentified cyclic materials.

Iron(II) sulfate reduction of the butenyl compounds produced starkly different results (Scheme 3). Treatment of the *cis*-isomer **5b** gave the pyrroline **4b** in 83% yield, however the *trans* compound **6b** gave the pyrroline **4b** in only 14% yield, accompanied by the pyrrolizidine **8** (46%). This bicyclic compound arises from initial 5-*exo-trig* cyclisation of the aminyl radical onto the alkene, followed by a subsequent attack of the intermediate carbon-centred radical on the phenyl ring leading to migration of the aromatic group (Scheme 3). Such phenyl migrations under radical conditions have been observed by Aubé[17] and, in another sense, by Sherburn.[18] The structure of the pyrrolizidine **8** was established using NMR correlation techniques including COSY, HMQC and HMBC experiments. The stereochemistry at the newly created stereogenic centre can be predicted by consideration of two possible transition states. In the Beckwith model for 5-*exo-trig* radical cyclisations,[19] a chair-like transition state is preferred over the boat-like alternative, and bulky substituents (such as the sterically demanding ethyl ester) should preferentially be pseudoequatorial in the newly developing ring (Figure 4). This chair-like transition state



Scheme 3

also leaves the intermediate radical more suitably disposed for the subsequent attack on the neighbouring phenyl group.

Reaction of the butenyl isomers with Bu_3SnH also gave different results – the *cis* isomer **5b** gave mostly pyrroline **4b**, whereas the *trans* isomer **6b** gave pyrroline **4b**, accompanied by pyrrolizidine **8**. Use of $[Cu(PPh_3)Cl]_4$ gave the cleanest reactions: the *cis* isomer **5b** gave the pyrroline **4b** exclusively, while the *trans* isomer **6b** gave pyrrolizidine **8** in 89% yield.

Reactions of all other *cis* isomers **5c**–**e** with iron(II), Bu_3SnH, or $[Cu(PPh_3)Cl]_4$ gave the pyrrolines **4c**–**e**, respectively, in high yields, with no evidence of other cyclic products. Deoxygenation to give the pyrroline was also the major pathway for the *trans* isomers **6c** and **6d**, with some evidence for formation of other cyclic products. While the ^1H NMR spectra of the cyclic material arising from pentenyl compound **6c** showed some similarities to the pyrrolizidine **8**, the absence of a pair of doublets of doublets required for the benzylic CH_2 (an ABX system) makes the indolizidine **9** unlikely (Scheme 4). In fact, the initial *6-exo-trig* aminyl radical cyclisation is somewhat less favourable, as these cyclisations are usually much slower than the corresponding *5-exo-trig* cyclisations.[20]

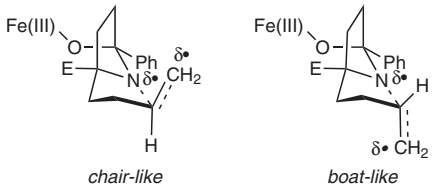
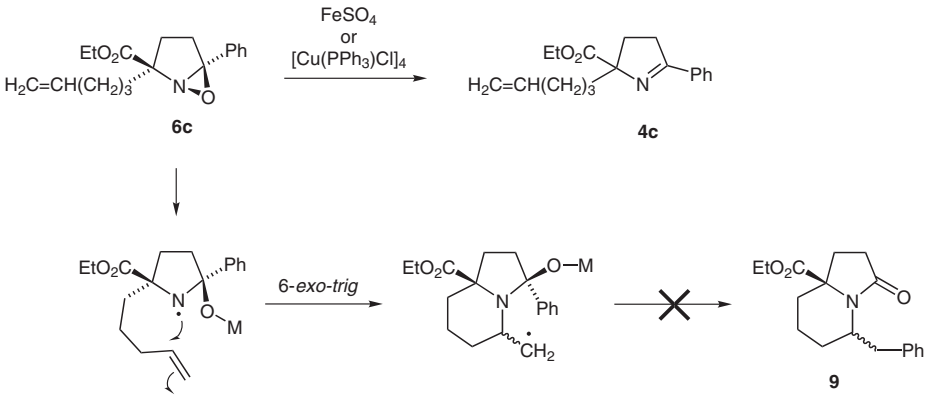


Figure 4 Possible transition states leading to pyrrolizidine **8**

The successful cyclisation of the *trans*-butenyl isomer **6b** led to investigation of the dimethyl analogue **6e**. Treatment of oxaziridine **6e** with $[Cu(PPh_3)Cl]_4$ gave an excellent yield (89%) of the aziridine **10** as the sole product of the reaction (Scheme 5). The reaction presumably follows a similar path initially: reductive cleavage of the N–O bond, followed by 5-*exo* cyclisation onto the alkene to generate a tertiary radical. This more hindered radical is less able to attack the aromatic ring, and therefore phenyl migration does not occur and the pyrrolizidine **11** is not formed. Instead, the result is cleavage of the five-mem-



Scheme 4

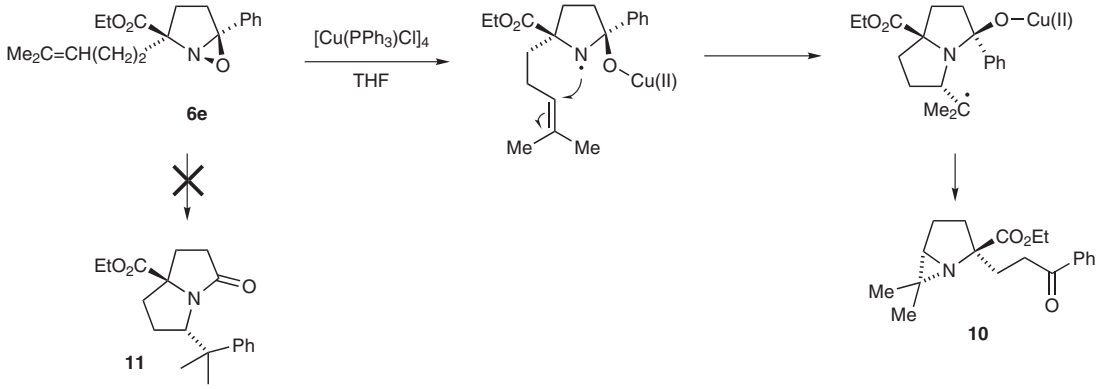
Table 3 Reductions of Oxaziridines

Alkenyl chain	Oxaziridine (*cis/trans*)	Reducing agent	Recovered starting material (%)	Pyrroline (%)	Other products (%)
$CH_2CH=CH_2$	**5a** (*cis*)	$FeSO_4$	0	39	pyrrole **7** (32)
		Bu_3SnH	76	12	–
		$[Cu(PPh_3)Cl]_4$	0	34	pyrrole **7** (44)
	6a (*trans*)	$FeSO_4$	0	38	pyrrole **7** (30), unidentified cyclic products (ca. 10)
		Bu_3SnH	66	16	pyrrole **7** (1.5)
		$[Cu(PPh_3)Cl]_4$	0	29	pyrrole **7** (41), unidentified cyclic products (ca. 15)
$(CH_2)_2CH=CH_2$	**5b** (*cis*)	$FeSO_4$	0	83	–
		Bu_3SnH	21	71	–
		$[Cu(PPh_3)Cl]_4$	0	92	–
	6b (*trans*)	$FeSO_4$	0	14	pyrrolizidine **8** (46)
		Bu_3SnH	16	44	pyrrolizidine **8** (20)
		$[Cu(PPh_3)Cl]_4$	0	0	pyrrolizidine **8** (89)
$(CH_2)_3CH=CH_2$	**5c** (*cis*)	$FeSO_4$	0	89	–
		Bu_3SnH	0	84	–
		$[Cu(PPh_3)Cl]_4$	0	81	–
	6c (*trans*)	$FeSO_4$	0	66	unidentified cyclic products (ca. 26)
		Bu_3SnH	0	82	—
		$[Cu(PPh_3)Cl]_4$	0	41	unidentified cyclic products (ca. 40)
$(CH_2)_4CH=CH_2$	**5d** (*cis*)	$FeSO_4$	0	94	–
	6d (*trans*)	$FeSO_4$	0	92	–
$(CH_2)_4CH=CMe_2$	**5e** (*cis*)	$[Cu(PPh_3)Cl]_4$	0	87	–
	6e (*trans*)	$[Cu(PPh_3)Cl]_4$	0	0	aziridine **10** (89)

bered ring and accompanying cyclisation to give the aziridine **10**.

The final challenge was an attempt to effect radical reactions in the absence of metal-containing reagents. *p*-Toluenesulfonyl iodide (tosyl iodide) has proved a useful reagent for sulfone-directed synthesis of nitrogen[21] and oxygen[22] heterocycles, and reports of its involvement in single electron transfer processes[23] prompted us to investigate its reaction with the alkenyl oxaziridines **5** and **6**. While there was evidence in the ^1H NMR spectra of the crude reaction mixtures that addition to the alkene had occurred, unfortunately the reactions gave complex mixtures and no useful products could be obtained.

In this study we have shown that stereoselective formation of oxaziridines can be achieved by variation of reaction conditions, and the isomeric oxaziridines can be used as aminyl radical precursors. While the *cis* compounds **5**, on treatment with a suitable reducing agent, generally gave products resulting from deoxygenation, the *trans* isomers **6b** and **6e** led to products that could only have arisen from intermediate aminyl radicals undergoing a 5-*exo-trig* cyclisation onto a pendant alkenyl chain. There is a clear stereochemical demand in these reactions for the alkenyl chain to be *trans* to the breaking N–O bond for cyclisations to occur. The particularly successful formation of the bicyclic compounds **8** and **10** suggests that this procedure could be useful for the synthesis of a range of alkaloid derivatives.



Scheme 5

Melting points are uncorrected. IR spectra were recorded using a Hitachi model EPI-G spectrophotometer and refer to thin films of liquids or paraffin mulls of solids between KBr plates. Absorptions of medium to strong intensity only are reported here in cm^{-1}. ^1H NMR (300 MHz) and ^{13}C (75.5 MHz) NMR spectra were recorded using a Bruker CXP300 instrument as $CDCl_3$ solutions. Chemical shifts are reported in parts per million downfield from tetramethylsilane (internal references: $\delta_H = 7.26$ relative to residual $CHCl_3$; $\delta_C = 77.04$ relative to the central peak of the $CDCl_3$ triplet). ^{13}C NMR assignments were made using DEPT spectra, and Ar_C refers to a quaternary aromatic carbon and Ar_{CH} refers to an aromatic carbon bearing one hydrogen. Mass spectra, in electron ionisation mode, were obtained using an AEI MS12 instrument with 8000 V accelerating voltage and with an ion source temperature of 200 °C. Elemental analyses were performed by the School of Chemistry Microanalysis Service, UNSW. Reagents and solvents were purified where necessary by standard procedures.

Alkylation of Nitrone 1; General Procedure

NaH (0.07 g of an 80% dispersion in paraffin oil, 2.36 mmol) was added to a stirred solution of ethyl 2-phenyl-1-pyrroline-5-carboxylate 1-oxide (**1**; 0.50 g, 2.15 mmol) in anhyd THF (10 mL) at r.t. After 5 min, DMF (0.5 mL) was added, and stirring was continued for a further 5 min, whereupon the desired alkylating agent (2.15 mmol) was added slowly over 10 min. Stirring was continued for 24 to 48 h, when H_2O (1 mL) was added. The mixture was concentrated under reduced pressure, and the product was extracted into $CHCl_3$ (3×15 mL). The combined organic extracts were dried ($MgSO_4$), concentrated under reduced pressure and purified by flash chromatography (Et_2O–light petroleum as eluent) to give the pure C-5 substituted nitrone **3**.

Ethyl 2-Phenyl-5-(prop-2′-en-1′-yl)-1-pyrroline-5-carboxylate 1-Oxide (3a)

Waxy yellow solid; yield: 390 mg (66%); mp 46 °C.

IR (paraffin): 1735, 1543, 1360, 1275, 1250, 1205, 1175, 1120, 1068, 1025, 910, 760 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 1.25 (t, J = 7.1 Hz, 3 H, CH_3), 2.21–2.43 (m, 2 H, H-4), 2.76 (dd, J = 14.3, 8.5 Hz, 1 H, H-1′a), 2.99–3.20 (m, 3 H, H-1′b, H-3), 4.16–4.30 (m, 2 H, OCH_2), 5.16 (d, J = 10.0 Hz, 1 H, H-3′a), 5.22 (d, J = 17.2 Hz, 1 H, H-3′b), 5.63–5.71 (m, 1 H, H-2′), 7.41–7.44 (m, 3 H, ArH), 8.33–8.36 (m, 2 H, ArH).

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 13.8 (CH_3), 25.2 (CH_2), 28.3 (CH_2), 37.4 (CH_2), 61.9 (OCH_2), 84.1 (C-5), 120.5 (C-3′), 127.2 (Ar_{CH}), 128.2 (Ar_{CH}), 129.1 (C-2), 130.3 (C-2′), 131.3 (Ar_{CH}), 141.3 (Ar_C), 170.0 (C=O).

MS (EI): m/z = 273 (M, 28%).

Anal. Calcd for $C_{16}H_{19}NO_3$: C, 70.3; H, 7.0; N, 5.1. Found: C, 70.1; H, 7.1; N, 5.1.

Ethyl 5-(But-3′-en-1′-yl)-2-phenyl-1-pyrroline-5-carboxylate 1-Oxide (3b)

Waxy yellow solid; yield: 443 mg (72%); mp 52 °C.

IR (paraffin): 1740, 1550, 1360, 1275, 1180, 720, 650 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 1.25 (t, J = 7.1 Hz, 3 H, CH_3), 2.06–2.29 (m, 4 H, H-1′, H-4), 2.37–2.53 (m, 2 H, H-2′), 3.04–3.25 (m, 2 H, H-3), 4.17–4.30 (m, 2 H, OCH_2), 4.96 (d, J = 10.3 Hz, 1 H, H-4′a) 5.05 (dd, J = 17.0, 1.6 Hz, 1 H, H-4′b), 5.83 (ddt, J = 17.0, 10.3, 6.3 Hz, 1 H, H-3′), 7.41–7.46 (m, 3 H, ArH), 8.34–8.37 (m, 2 H, ArH).

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 13.9 (CH_3), 26.0 (CH_2), 27.4 (CH_2), 28.5 (CH_2), 32.5 (CH_2), 62.0 (OCH_2), 83.9 (C-5), 115.2 (C-4′), 127.4 (Ar_{CH}), 128.4 (Ar_{CH}), 129.0 (C-2), 130.5 (Ar_{CH}), 137.2 (C-3′), 141.1 (Ar_C), 170.2 (C=O).

MS (EI): m/z = 287 (M, 8%).

Anal. Calcd for $C_{17}H_{21}NO_3$: C, 71.1; H, 7.4; N, 4.9. Found: C, 70.8; H, 7.5; N, 4.8.

Ethyl 5-(Pent-4′-en-1′-yl)-2-phenyl-1-pyrroline-5-carboxylate 1-Oxide (3c)

Colourless waxy solid; yield: 712 mg (81%); mp 52 °C.

IR (paraffin): 1735, 1645, 1570, 1545, 1280, 1250, 1210, 1080, 900, 700, 680 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 1.24 (t, J = 7.2 Hz, 3 H, CH_3), 1.26–1.39 (m, 2 H, H-2′), 2.07–2.31 (m, 5 H, H-1′, H-3′, H-4a), 2.42–2.49 (m, 1 H, H-4b), 3.08–3.20 (m, 2 H, H-3), 4.15–4.28 (m, 2 H, OCH_2), 4.93 (d, J = 10.3 Hz, 1 H, H-5′a), 4.99 (d, J = 17.2 Hz, 1 H, H-5′b), 5.72–5.78 (m, 1 H, H-4′), 7.40–7.43 (m, 3 H, ArH), 8.33–8.36 (m, 2 H, ArH).

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 13.9 (CH_3), 22.4 (CH_2), 26.0 (CH_2), 28.5 (CH_2), 32.9 (CH_2), 33.6 (CH_2), 62.0 (OCH_2), 84.1 (C-5), 115.0 (C-5′), 127.3 (Ar_{CH}), 128.4 (Ar_{CH}), 129.1 (C-2), 130.4 (Ar_{CH}), 137.9 (C-4′), 141.3 (Ar_C), 170.4 (C=O).

MS (EI): m/z = 301 (M, 10%).

Anal. Calcd for $C_{18}H_{23}NO_3$: C, 71.7; H, 7.7; N, 4.65. Found: C, 72.0; H, 7.8; N, 4.6.

Ethyl 5-(Hex-5′-en-1′-yl)-2-phenyl-1-pyrroline-5-carboxylate 1-Oxide (3d)

Waxy yellow solid; yield: 530 mg (79%); mp 48–49 °C.

IR (paraffin): 1745, 1640, 1575, 1540, 1260, 1220, 1180, 1020, 910, 850, 760, 690 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.22 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.35–1.52 (m, 4 H, H-2′, H-3′), 1.98–2.24 (m, 5 H, H-1′, H-4′, H-4a), 2.39–2.48 (m, 1 H, H-4b), 3.01–3.18 (m, 2 H, H-3), 4.13–4.26 (m, 2 H, OCH_2) 4.86–4.97 (m, 2 H, H-6′), 5.69–5.77 (m, 1 H, H-5′), 7.39–7.42 (m, 3 H, ArH), 8.31–8.34 (m, 2 H, ArH).

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 13.9 (CH_3), 22.3 (CH_2), 25.9 (CH_2), 28.4 (CH_2), 28.8 (CH_2), 33.2 (CH_2), 33.3 (CH_2), 61.9 (OCH_2), 84.1 (C-5), 114.4 (C-6′), 127.3 (Ar_{CH}), 128.3 (Ar_{CH}), 129.1 (C-2), 130.4 (Ar_{CH}), 138.4 (C-5′), 142.7 (Ar_C), 170.4 (C=O).

MS (EI): *m*/*z* = 315 (M, 15%).

Anal. Calcd for $C_{19}H_{25}NO_3$: C, 72.35; H, 8.0; N, 4.4. Found: C, 72.4; H, 7.8; N, 4.25.

Ethyl 5-(4′-Methylpent-3′-en-1′-yl)-2-phenyl-1-pyrroline-5-carboxylate 1-Oxide (3e)

Waxy yellow solid; yield: 699 mg (from 500 mg of **1**, 69%); mp 50–52 °C.

IR (paraffin): 1730, 1540, 1210, 1160, 930, 755, 690 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.27 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3), 1.58 (s, 3 H, $=CCH_3$), 1.64 (s, 3 H, $=CCH_3$), 1.92–2.35 (m, 5 H, H-1′, H-2′, H-4a), 2.46–2.54 (m, 1 H, H-4b), 3.10–3.23 (m, 2 H, H-3), 4.17–4.30 (m, 2 H, OCH_2), 5.10–5.18 (m, 1 H, H-3′), 7.41–7.46 (m, 3 H, ArH), 8.35–8.38 (m, 2 H, ArH).

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 14.0 (CH_2CH_3), 17.7 ($=CCH_3$), 21.9 (CH_2), 25.6 ($=CCH_3$), 26.1 (CH_2), 28.5 (CH_2), 33.4 (CH_2), 62.0 (OCH_2), 84.0 (C-5), 122.9 (C-3′), 127.4 (Ar_{CH}), 128.4 (Ar_{CH}), 129.2 (C-2), 130.4 (Ar_{CH}), 132.5 (C-4′), 141.0 (Ar_C), 170.4 (C=O).

MS (EI): *m*/*z* = 315 (M, 4%).

Anal. Calcd for $C_{19}H_{25}NO_3$: C, 72.35; H, 8.0; N, 4.4. Found: C, 72.3; H, 8.3; N, 4.1.

Alkylation of Pyrroline 2; General Procedure

Ethyl 2-phenyl-1-pyrroline-5-carboxylate (**2**; 1.00 g, 4.61 mmol) was dissolved in anhyd THF (10 mL) at r.t., and DMF (1 mL) was added followed by NaH (152 mg of an 80% dispersion in paraffin oil, 5.10 mmol). The cloudy yellow solution was stirred for 10 min and then the appropriate alkylating agent (5.76 mmol) was added, and the mixture was stirred under N_2 overnight. The mixture was concentrated under reduced pressure, and the residue was partitioned between H_2O and CH_2Cl_2. The aqueous layer was extracted with CH_2Cl_2 (2 × 5 mL), and the combined organic extracts were dried ($MgSO_4$), concentrated under reduced pressure and purified by flash chromatography (Et_2O–light petroleum as eluent) to give the pure C-5 substituted pyrroline **4**.

Ethyl 2-Phenyl-5-(prop-2′-en-1′-yl)-1-pyrroline-5-carboxylate (4a)

Yellow oil; yield: 1.10 g (92%).

IR (film): 1735, 1615, 1450, 1375, 910, 755, 690 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.23 (t, *J* = 7.1 Hz, 3 H, CH_3), 1.98 (ddd, *J* = 13.3, 9.6, 6.5 Hz, 1 H, H-4a), 2.40 (ddd, *J* = 13.3, 9.9, 5.8 Hz, 1 H, H-4b), 2.61–2.75 (m, 2 H, H-1′), 2.88–3.10 (m, 2 H, H-3), 4.16 (q, *J* = 7.1 Hz, 2 H, OCH_2), 5.03–5.13 (m, 2 H, H-3′), 5.64–5.78 (m, 1 H, H-2′), 7.31–7.43 (m, 3 H, ArH), 7.82–7.84 (m, 2 H, ArH).

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 14.2 (CH_3), 30.4 (CH_2), 35.1 (CH_2), 42.7 (CH_2), 61.1 (OCH_2), 83.1 (C-5), 118.7 (C-3′), 128.0 (Ar_{CH}), 128.3 (Ar_{CH}), 130.8 (Ar_{CH}), 133.1 (C-2′), 134.0 (Ar_C), 173.9 (C-2 or C=O), 174.3 (C=O or C-2).

MS (EI): *m*/*z* = 257 (M, 15%).

Anal. Calcd for $C_{16}H_{19}NO_2$: C, 74.7; H, 7.4; N, 5.4. Found: C, 74.75; H, 7.3; N, 5.3.

Ethyl 5-(But-3′-en-1′-yl)-2-phenyl-1-pyrroline-5-carboxylate (4b)

Yellow oil; yield: 1.10 g (89%).

IR (film): 1740, 1630, 1410, 1380, 1320, 1200, 780, 680 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.25 (t, *J* = 7.1 Hz, 3 H, CH_3), 1.93–2.20 (m, 5 H, H-1′, H-2′, H-4′a), 2.48 (ddd, *J* = 13.3, 9.7, 5.6 Hz, 1 H, H-4′b), 3.00–3.09 (m, 2 H, H-3), 4.19 (q, *J* = 7.1 Hz, 2 H, OCH_2), 4.93 (d, *J* = 10.3 Hz, 1 H, H-4′a), 5.02 (d, *J* = 17.4 Hz, 1 H, H-4′b), 5.75–5.90 (m, 1 H, H-3′), 7.36–7.43 (m, 3 H, ArH), 7.85–7.88 (m, 2 H, ArH).

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 14.1 (CH_3), 28.7 (CH_2), 31.4 (CH_2), 35.5 (CH_2), 37.9 (CH_2), 60.9 (OCH_2), 83.1 (C-5), 114.5 (C-4′), 127.9 (Ar_{CH}), 128.3 (Ar_{CH}), 130.7 (Ar_{CH}), 134.0 (Ar_C), 138.0 (C-2′), 173.9 (C-2 or C=O), 174.1 (C=O or C-2).

MS (EI): *m*/*z* = 271 (M, 16%).

Anal. Calcd for $C_{17}H_{21}NO_2$: C, 75.25; H, 7.8; N, 5.2. Found: C, 75.2; H, 7.9; N, 4.9.

Ethyl 5-(Pent-4′-en-1′-yl)-2-phenyl-1-pyrroline-5-carboxylate (4c)

Yellow oil; yield: 1.18 g (90%).

IR (film): 1735, 1640, 1400, 1365, 1325, 780, 690 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.26 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.42–1.55 (m, 2 H, H-2′), 1.93–2.02 (m, 3 H, H-1′, H-4a), 2.09 (q, *J* = 7.2 Hz, 2 H, H-3′), 2.43–2.51 (m, 1 H, H-4b), 3.01–3.09 (m, 2 H, H-3), 4.21 (q, *J* = 7.0 Hz, 2 H, OCH_2), 4.93–5.03 (m, 2 H, H-5′), 5.74–5.85 (m, 1 H, H-4′), 7.37–7.44 (m, 3 H, ArH), 7.86–7.89 (m, 2 H, ArH).

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 14.2 (CH_3), 23.7 (CH_2), 31.4 (CH_2), 33.9 (CH_2), 35.5 (CH_2), 38.3 (CH_2) 61.0 (OCH_2), 83.5 (C-5), 114.7 (C-5′), 128.0 (Ar_{CH}), 128.3 (Ar_{CH}), 130.7 (Ar_{CH}), 134.1 (Ar_C), 138.4 (C-4′), 173.7 (C-2 or C=O), 174.3 (C=O or C-2).

MS (EI): *m*/*z* = 285 (M, 5%).

Anal. Calcd for $C_{18}H_{23}NO_2$: C, 75.8; H, 8.1; N, 4.9. Found: C, 76.2; H, 8.2; N, 4.6.

Ethyl 5-(Hex-5′-en-1′-yl)-2-phenyl-1-pyrroline-5-carboxylate (4d)

Yellow oil; yield: 1.12 g (82%).

IR (film): 1705, 1630, 1420, 1355, 1215, 760, 710, 690 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.26 (t, *J* = 7.1 Hz, 3 H, CH_3), 1.30–1.45 (m, 4 H, H-2′, H-3′), 1.88–2.09 (m, 5 H, H-1′, H-4′, H-4a), 2.48 (ddd, *J* = 13.3, 9.7, 5.6 Hz, 1 H, H-4b), 3.00–3.08 (m, 2 H, H-3), 4.21 (q, *J* = 7.1 Hz, 2 H, OCH_2), 4.90–5.01 (m, 2 H, H-6′), 5.72–5.83 (m, 1 H, H-5′), 7.37–7.45 (m, 3 H, ArH), 7.86–7.89 (m, 2 H, ArH).

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 14.2 (CH_3), 23.8 (CH_2), 29.2 (CH_2), 31.3 (CH_2), 33.5 (CH_2), 35.5 (CH_2), 38.7 (CH_2) 61.0 (OCH_2), 83.6 (C-5), 114.4 (C-6′), 128.0 (Ar_{CH}), 128.3 (Ar_{CH}), 130.7 (Ar_{CH}), 134.1 (Ar_C), 138.8 (C-5′), 173.7 (C-2 or C=O), 174.4 (C=O or C-2).

MS (EI): *m*/*z* = 299 (M, 8%).

Anal. Calcd for $C_{19}H_{25}NO_2$: C, 76.2; H, 8.4; N, 4.7. Found: C, 76.1; H, 8.2; N, 4.5.

Ethyl 5-(4′-Methylpent-3′-en-1′-yl)-2-phenyl-1-pyrroline-5-carboxylate (4e)

Viscous colourless oil; yield: 602 mg (from 500 mg of **2**, 83%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.28 (t, *J* = 7.2 Hz, 3 H, CH_2CH_3), 1.59 (s, 3 H, $=CCH_3$), 1.66 (s, 3 H, $=CCH_3$), 1.92–2.09 (m, 5 H, H-1′, H-2′, H-4a), 2.48 (ddd, *J* = 13.2, 9.6, 6.0 Hz, 1 H, H-4b), 3.01–

3.09 (m, 2 H, H-3), 4.21 (q, J = 7.2 Hz, 2 H, OCH_2), 5.07–5.14 (m, 1 H, H-3′), 7.37–7.44 (m, 3 H, ArH), 7.86–7.92 (m, 2 H, ArH).

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 14.2 (CH_2CH_3), 17.6 (=CCH_3), 23.2 (CH_2), 25.6 (=CCH_3), 31.4 (CH_2), 35.5 (CH_2), 38.9 (CH_2), 61.0 (OCH_2), 83.4 (C-5), 123.7 (C-3′), 128.0 (Ar_{CH}), 128.3 (Ar_{CH}), 130.7 (Ar_{CH}), 131.9 (C-4′), 134.2 (Ar_C), 173.8 (C-2 or C=O), 174.2 (C=O or C-2).

Anal. Calcd for $C_{19}H_{25}NO_2$: C, 76.2; H, 8.4; N, 4.7. Found: C, 75.8; H, 8.3; N, 4.3.

Irradiation of Nitrones 3; General Procedure

A solution of the appropriate nitrone **3** (0.97 mmol) in anhyd, degassed benzene (20 mL) was placed in a quartz tube in a fan-cooled Oliphant 'Merry-Go-Round' reactor equipped with an ultraviolet lamp. The solution was irradiated for 16 h, and the solvent was removed to give the crude mixture of oxaziridines which was purified by preparative TLC using Et_2O–light petroleum as the eluent. The yields of isomeric oxaziridines **5** and **6** are given in Table 1. The *cis* isomers **5** routinely migrated with higher R_f than the *trans* isomers **6**.

Oxidation of 1-Pyrrolines 4 with Peracid; General Procedure

The appropriate 1-pyrroline **4** (0.97 mmol) in MeOH (5 mL) was treated with magnesium monoperoxyphthalate (240 mg, 0.48 mmol) in MeOH (5 mL) and the solution was stirred for 30 min at r.t. A dilute aq solution of Na_2SO_3 (2 mL) was added, and the MeOH was removed under reduced pressure. The aqueous residue was extracted with CH_2Cl_2 (2 × 5 mL). The combined organic extracts were washed with aq $NaHCO_3$ (2 × 5 mL) and then H_2O, and the organic layer was dried ($MgSO_4$) and evaporated to dryness under reduced pressure. The crude mixture of isomeric oxaziridines was separated by preparative TLC using Et_2O–light petroleum as eluent. The yields of isomeric oxaziridines **5** and **6** are given in Table 2.

Ethyl *cis*-5-Phenyl-2-(prop-2′-en-1′-yl)-6-oxa-1-azabicyclo[3.1.0]hexane-2-carboxylate (5a)

Yellow oil.

IR (film): 1725, 1010, 920, 890 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.20 (t, J = 7.3 Hz, 3 H, CH_3), 1.74 (ddd, J = 13.3, 10.7, 8.2 Hz, 1 H, H-4a), 2.05 (dd, J = 13.3, 8.2 Hz, 1 H, H-4b), 2.50–2.77 (m, 4 H, H-3, H-1′), 4.13–4.23 (m, 2 H, OCH_2), 5.13 (dd, J = 10.3, 1.0 Hz, 1 H, H-3′a), 5.20 (d, J = 16.9 Hz, 1 H, H-3′b), 5.93 (m, 1 H, H-2′), 7.36–7.38 (m, 3 H, ArH), 7.52–7.55 (m, 2 H, ArH).

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 14.0 (CH_3), 29.2 (CH_2), 29.7 (CH_2), 39.5 (CH_2), 61.4 (OCH_2), 76.7 (C-2), 88.6 (C-5), 118.5 (C-3′), 126.9 (Ar_{CH}), 128.3 (Ar_{CH}), 129.3 (Ar_{CH}), 133.0 (C-2′), 134.7 (Ar_C), 171.3 (C=O).

MS (EI): m/z = 273 (M, 8%).

Anal. Calcd for $C_{16}H_{19}NO_3$: C, 70.3; H, 7.0; N, 5.1. Found: C, 70.8; H, 7.2; N, 5.0.

Ethyl *trans*-5-Phenyl-2-(prop-2′-en-1′-yl)-6-oxa-1-azabicyclo[3.1.0]hexane-2-carboxylate (6a)

Yellow oil.

IR (film): 1730, 1640, 1360, 1340, 1175, 1080, 920, 840 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.29 (t, J = 7.2 Hz, 3 H, CH_3), 1.87 (dd, J = 13.3, 8.2 Hz, 1 H, H-4a), 2.19 (ddd, J = 13.3, 10.5, 8.5 Hz, 1 H, H-4b), 2.34–2.50 (m, 2 H, H-3 or H-1′), 2.58 (dd, J = 13.8, 7.2 Hz, 1 H, H-3 or H-1′), 2.66 (dd, J = 14.3, 8.0 Hz, 1 H, H-3 or H-1′), 4.18–4.34 (m, 2 H, OCH_2), 5.07–5.14 (m, 2 H, H-3′), 5.64–5.78 (m, 1 H, H-2′), 7.31–7.36 (m, 3 H, ArH), 7.44–7.50 (m, 2 H, ArH).

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 14.3 (CH_3), 26.6 (CH_2), 27.8 (CH_2), 39.5 (CH_2), 61.5 (OCH_2), 76.6 (C-2), 88.1 (C-5), 119.6 (C-3′), 127.1 (Ar_{CH}), 128.3 (Ar_{CH}), 129.5 (Ar_{CH}), 131.5 (C-2′), 134.5 (Ar_C), 171.4 (C=O).

MS (EI): m/z = 273 (M, 22%).

Anal. Calcd for $C_{16}H_{19}NO_3$: C, 70.3; H, 7.0; N, 5.1. Found: C, 70.75; H, 7.2; N, 4.8.

Ethyl *cis*-2-(But-3′-en-1′-yl)-5-phenyl-6-oxa-1-azabicyclo[3.1.0]hexane-2-carboxylate (5b)

Yellow oil.

IR (film): 1730, 1650, 1545, 1420, 1270, 1150, 895, 820 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.34 (t, J = 7.1 Hz, 3 H, CH_3), 1.75 (ddd, J = 13.5, 11.6, 5.1 Hz, 1 H), 1.84–1.96 (m, 2 H), 2.09–2.27 (m, 3 H), 2.47 (ddd, J = 14.5, 10.5, 8.6 Hz, 1 H), 2.72 (dd, J = 14.5, 8.3 Hz, 1 H), 4.25–4.36 (m, 2 H, OCH_2), 4.94–5.04 (m, 2 H, H-4′), 5.69–5.83 (m, 1 H, H-3′), 7.35–7.40 (m, 3 H, ArH), 7.50–7.54 (m, 2 H, ArH).

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 14.3 (CH_3), 27.5 (CH_2), 27.8 (CH_2), 28.5 (CH_2), 34.3 (CH_2), 61.4 (OCH_2), 76.6 (C-2), 87.9 (C-5), 115.3 (C-4′), 127.2 (Ar_{CH}), 128.4 (Ar_{CH}), 129.6 (Ar_{CH}), 134.6 (Ar_C), 137.1 (C-3′), 171.8 (C=O).

MS (EI): m/z = 287 (M, 2%).

Anal. Calcd for $C_{17}H_{21}NO_3$: C, 71.1; H, 7.4; N, 4.9. Found: C, 71.4; H, 7.5; N, 4.7.

Ethyl *trans*-2-(But-3′-en-1′-yl)-5-phenyl-6-oxa-1-azabicyclo[3.1.0]hexane-2-carboxylate (6b)

Yellow oil.

IR (film): 3040, 2990, 2820, 1725, 1010, 920, 890 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.25 (t, J = 7.2 Hz, 3 H, CH_3), 1.70 (ddd, J = 13.1, 10.5, 8.2 Hz, 1 H), 1.81–2.15 (m, 5 H), 2.51 (ddd, J = 14.4, 10.2, 8.2 Hz, 1 H), 2.64 (dd, J = 14.4, 7.7 Hz, 1 H), 4.14–4.26 (m, 2 H, OCH_2), 4.97 (dd, J = 10.2, 2.0 Hz, 1 H, H-4′a), 5.00–5.07 (m, 1 H, H-4′b), 5.78–5.87 (m, 1 H, H-3′), 7.36–7.39 (m, 3 H, ArH), 7.52–7.57 (m, 2 H, ArH).

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 14.1 (CH_3), 29.2 (CH_2), 29.4 (CH_2), 30.5 (CH_2), 34.5 (CH_2), 61.3 (OCH_2), 76.7 (C-2), 88.6 (C-5), 114.7 (C-4′), 126.9 (Ar_{CH}), 128.3 (Ar_{CH}), 129.3 (Ar_{CH}), 134.8 (Ar_C), 138.0 (C-3′), 171.7 (C=O).

MS (EI): m/z = 287 (M, 2%).

Anal. Calcd for $C_{17}H_{21}NO_3$: C, 71.1; H, 7.4; N, 4.9. Found: C, 71.0; H, 7.5; N, 4.75.

Ethyl *cis*-2-(Pent-4′-en-1′-yl)-5-phenyl-6-oxa-1-azabicyclo[3.1.0]hexane-2-carboxylate (5c)

Yellow oil.

IR (film): 1725, 1640, 1600, 1540, 1420, 1350, 1240, 1190, 980, 890, 700 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.36 (t, J = 7.2 Hz, 3 H, CH_3), 1.42–1.70 (m, 3 H), 1.79–1.89 (m, 2 H), 2.04 (br q, J = 7.2 Hz, 2 H), 2.12–2.24 (m, 1 H), 2.41–2.50 (m, 1 H), 2.72 (dd, J = 14.9, 8.2 Hz, 1 H), 4.26–4.33 (m, 2 H, OCH_2), 4.92–5.01 (m, 2 H, H-5′), 5.68–5.74 (m, 1 H, H-4′), 7.37–7.41 (m, 3 H, ArH), 7.50–7.54 (m, 2 H, ArH).

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 14.1 (CH_3), 24.3 (CH_2), 29.1 (CH_2), 30.5 (CH_2), 33.8 (CH_2), 34.8 (CH_2), 61.2 (OCH_2), 76.8 (C-2), 88.5 (C-5), 114.7 (C-5′), 126.9 (Ar_{CH}), 128.0 (Ar_{CH}), 129.2 (Ar_{CH}), 134.7 (Ar_C), 138.2 (C-4′), 171.9 (C=O).

MS (EI): m/z = 301 (M, 5%).

Anal. Calcd for $C_{18}H_{23}NO_3$: C, 71.7; H, 7.7; N, 4.65. Found: C, 71.5; H, 7.6; N, 4.5.

Ethyl *trans*-2-(Pent-4′-en-1′-yl)-5-phenyl-6-oxa-1-azabicyclo[3.1.0]hexane-2-carboxylate (6c)
Yellow oil.

IR (film): 1725, 1600, 1410, 1280, 1240, 1150, 880, 825 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 1.25 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.40–1.51 (m, 2 H), 1.71 (ddd, *J* = 13.3, 10.8, 8.2 Hz, 1 H), 1.78–2.15 (m, 5 H), 2.51 (ddd, *J* = 14.4, 10.8, 8.2 Hz, 1 H), 2.64 (dd, *J* = 14.4, 7.2 Hz, 1 H), 4.14–4.27 (m, 2 H, OCH_2), 4.95–5.08 (m, 2 H, H-5′), 5.78–5.87 (m, 1 H, H-4′), 7.36–7.39 (m, 3 H, ArH), 7.52–7.55 (m, 2 H, ArH).

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 14.2 (CH_3), 23.5 (CH_2), 27.3 (CH_2), 27.7 (CH_2), 33.6 (CH_2), 34.4 (CH_2), 61.2 (OCH_2), 76.8 (C-2), 87.8 (C-5), 114.7 (C-5′), 127.1 (Ar_{CH}), 128.0 (Ar_{CH}), 129.5 (Ar_{CH}), 134.6 (Ar_C), 137.6 (C-4′), 171.9 (C=O).

MS (EI): *m*/*z* = 301 (M, 3%).

Anal. Calcd for $C_{18}H_{23}NO_3$: C, 71.7; H, 7.7; N, 4.65. Found: C, 71.4; H, 7.6; N, 4.5.

Ethyl *cis*-2-(Hex-5′-en-1′-yl)-5-phenyl-6-oxa-1-azabicyclo[3.1.0]hexane-2-carboxylate (5d)
Yellow oil.

IR (film): 1725, 1595, 1395, 1325, 1230, 1000, 880, 810, 690 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 1.25 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.38–1.52 (m, 3 H), 1.65–1.75 (m, 2 H), 1.89–1.98 (m, 2 H), 2.03–2.10 (m, 3 H), 2.45–2.67 (m, 2 H), 4.14–4.27 (m, 2 H, OCH_2), 4.94 (dt, *J* = 10.3, 1.0 Hz, 1 H, H-6′a), 5.01 (br d, *J* = 17.2 Hz, 1 H, H-6′b), 5.77–5.86 (m, 1 H, H-5′), 7.36–7.39 (m, 3 H, ArH), 7.52–7.55 (m, 2 H, ArH).

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 14.2 (CH_3), 23.6 (CH_2), 27.2 (CH_2), 27.6 (CH_2), 28.9 (CH_2), 32.3 (CH_2), 35.0 (CH_2), 61.6 (OCH_2), 77.0 (C-2), 87.7 (C-5), 114.7 (C-6′), 127.1 (Ar_{CH}), 127.3 (Ar_{CH}), 129.5 (Ar_{CH}), 134.7 (Ar_C), 137.3 (C-5′), 172.0 (C=O).

MS (EI): *m*/*z* = 316 (M + 1, 1%).

Anal. Calcd for $C_{19}H_{25}NO_3$: C, 72.35; H, 8.0; N, 4.4. Found: C, 72.6; H, 8.1; N, 4.4.

Ethyl *trans*-2-(Hex-5′-en-1′-yl)-5-phenyl-6-oxa-1-azabicyclo[3.1.0]hexane-2-carboxylate (6d)
Yellow oil.

IR (film): 1725, 1620, 1535, 1420, 1365, 1240, 1190, 1020, 965, 890, 705 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 1.34 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.35–1.45 (m, 4 H), 1.58–1.66 (m, 1 H), 1.80–1.89 (m, 2 H), 2.02 (br q, *J* = 6.7 Hz, 2 H), 2.14–2.25 (m, 1 H), 2.45 (ddd, *J* = 14.4, 10.7, 8.7 Hz, 1 H), 2.71 (dd, *J* = 14.4, 8.2 Hz, 1 H), 4.25–4.33 (m, 2 H, OCH_2), 4.89–4.99 (m, 2 H, H-6′), 5.69–5.79 (m, 1 H, H-5′), 7.36–7.39 (m, 3 H, ArH), 7.50–7.53 (m, 2 H, ArH).

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 14.3 (CH_3), 23.8 (CH_2), 27.3 (CH_2), 27.8 (CH_2), 28.9 (CH_2), 33.3 (CH_2), 34.8 (CH_2), 61.3 (OCH_2), 76.9 (C-2), 87.8 (C-5), 114.7 (C-6′), 127.1 (Ar_{CH}), 128.3 (Ar_{CH}), 129.5 (Ar_{CH}), 134.7 (Ar_C), 138.3 (C-5′), 172.0 (C=O).

MS (EI): *m*/*z* = 316 (M + 1, 1%).

Anal. Calcd for $C_{19}H_{25}NO_3$: C, 72.35; H, 8.0; N, 4.4. Found: C, 72.7; H, 8.1; N, 4.3.

Ethyl *cis*-2-(4′-Methylpent-3′-en-1′-yl)-5-phenyl-6-oxa-1-azabicyclo[3.1.0]hexane-2-carboxylate (5e)
Yellow oil.

IR (film): 1725, 1440, 1350, 1260, 1215, 750, 690 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 1.35 (t, *J* = 7.2 Hz, 3 H, CH_2CH_3), 1.55 (s, 3 H, $=CCH_3$), 1.64 (s, 3 H, $=CCH_3$), 1.64–1.71 (m, 2 H), 1.79–1.92 (m, 2 H), 2.02–2.26 (m, 2 H), 2.46 (ddd, *J* = 14.4, 10.7, 8.7 Hz, 1 H), 2.72 (dd, *J* = 14.4, 8.0 Hz, 1 H), 4.25–4.36 (m, 2 H, OCH_2), 5.02–5.07 (m, 1 H, H-3′), 7.36–7.40 (m, 3 H, ArH), 7.51–7.54 (m, 2 H, ArH).

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 14.3 (CH_2CH_3), 17.5 ($=CCH_3$), 23.1 (CH_2), 25.5 ($=CCH_3$), 27.4 (CH_2), 27.8 (CH_2), 35.1 (CH_2), 61.3 (OCH_2), 76.8 (C-2), 87.9 (C-5), 122.8 (C-3′), 127.1 (Ar_{CH}), 128.3 (Ar_{CH}), 129.5 (Ar_{CH}), 132.8 (C-4′), 134.6 (Ar_C), 171.9 (C=O).

MS (EI): *m*/*z* = 315 (M, 1%).

Anal. Calcd for $C_{19}H_{25}NO_3$: C, 72.35; H, 8.0; N, 4.4. Found: C, 72.1; H, 8.3; N, 4.2.

Ethyl *trans*-2-(4′-Methylpent-3′-en-1′-yl)-5-phenyl-6-oxa-1-azabicyclo[3.1.0]hexane-2-carboxylate (6e)
Yellow oil.

IR (film): 1725, 1445, 1350, 1175, 1000, 740, 690 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 1.26 (t, *J* = 7.2 Hz, 3 H, CH_2CH_3), 1.64 (s, 3 H, $=CCH_3$), 1.69 (s, 3 H, $=CCH_3$), 1.60–1.76 (m, 2 H), 1.92–2.10 (m, 4 H), 2.51 (ddd, *J* = 14.4, 10.8, 8.2 Hz, 1 H), 2.64 (dd, *J* = 14.4, 7.2 Hz, 1 H), 4.15–4.27 (m, 2 H, OCH_2), 5.13–5.19 (m, 1 H, H-3′), 7.37–7.40 (m, 3 H, ArH), 7.53–7.56 (m, 2 H, ArH).

MS (EI): *m*/*z* = 315 (M, 1%).

Anal. Calcd for $C_{19}H_{25}NO_3$: C, 72.35; H, 8.0; N, 4.4. Found: C, 72.3; H, 8.25; N, 4.2.

Reaction of Oxaziridines with Iron(II) Sulfate; General Procedure
The desired oxaziridine **5** or **6** (250 mg) in absolute EtOH (5 mL) was treated with an equimolar amount of $FeSO_4$ and the mixture was refluxed for 24 h. The solvent was removed under reduced pressure and the resulting residue was partitioned between H_2O (5 mL) and CH_2Cl_2 (5 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 5 mL) and the combined organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure to give the crude reaction product. Purification was effected using preparative TLC with Et_2O–light petroleum as eluent. Results are given in Table 3.

Reaction of Oxaziridines with Tributyltin Hydride/AIBN; General Procedure
The desired oxaziridine **5** or **6** (250 mg) was dissolved in anhyd degassed benzene (5 mL) and Bu_3SnH (29 mg, 0.09 mmol, in a 0.2 M solution) was added by syringe to the stirred solution. A small portion (ca. 2 mg) of AIBN was added and the solution was heated at reflux under argon for 12 h. H_2O (1 mL) was added and the organic solvent was removed under reduced pressure. The residue was extracted with CH_2Cl_2 (3 × 5 mL) and the combined organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure to give the crude reaction product. Purification was effected using preparative TLC with Et_2O–light petroleum as eluent. Results are given in Table 3.

Reaction of Oxaziridines with Tetrameric Copper(I)triphenylphosphine Chloride [Cu(PPh$_3$)Cl]$_4$; General procedure
The desired oxaziridine **5** or **6** (250 mg) was dissolved in anhyd THF (5 mL), $[Cu(PPh_3)Cl]_4$ (5 mol%) was added and the solution was refluxed until the starting material had been consumed (24–48 h). The solvent was removed under reduced pressure and the resulting residue was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure to give the crude reaction product. Purification was

effected using preparative TLC with Et_2O–light petroleum as eluent. Results are given in Table 3.

Ethyl 8-Benzyl-1-azabicyclo[3.3.0]octan-2-one-5-carboxylate (8)

Pale-yellow oil; yield: 115 mg (46%).

IR (film): 3450, 1680, 1440, 1375, 1310, 1250, 1175, 1010, 790, 690 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 1.08–1.20 (m, 1 H, H-6a), 1.21 (t, *J* = 7.2 Hz, CH_3), 1.79 (dt, *J* = 12.3, 8.7 Hz, 1 H, H-4a), 1.88–2.08 (m, 3 H, H-6b, H-7), 2.29 (dd, *J* = 12.3, 7.7 Hz, 1 H, H-4b), 2.47 (dd, *J* = 16.4, 8.7 Hz, 1 H, H-3a), 2.73 (dddd, *J* = 16.4, 12.3, 7.7, 1.0 Hz, 1 H, H-3b), 2.89 (dd, *J* = 13.3, 8.2 Hz, 1 H, PhC*H*a), 3.44 (dd, *J* = 13.3, 3.6 Hz, 1 H, PhC*H*b), 3.92–3.99 (m, 1 H, H-8), 4.14 (q, *J* = 7.2 Hz, 2 H, OCH_2), 7.13–7.30 (m, 5 H, ArH).

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 14.0 (CH_3), 31.6 (C-7), 31.9 (C-4), 32.5 (C-6), 36.0 (Ph*C*H_2), 36.2 (C-3), 54.3 (C-8), 61.5 (OCH_2), 75.7 (C-5), 126.2 (Ar_{CH}), 128.1 (Ar_{CH}), 129.5 (Ar_{CH}), 137.8 (Ar_C), 172.4 (NC=O), 173.6 (OC=O).

MS (EI): *m*/*z* = 288 (M + 1, 7%).

Anal. Calcd for $C_{17}H_{21}NO_3 \cdot 0.5H_2O$: C, 68.9; H, 7.5; N, 4.7. Found: C, 69.3; H, 7.2; N, 4.4.

Ethyl 6,6-Dimethyl-2-(3′-phenyl-3′-oxoprop-1′-yl)-1-azabicyclo[3.1.0]hexane-2-carboxylate (10)

Yellow-green oil; yield: 222 mg (46%).

IR (film): 3400, 1690, 1640, 1420, 1260, 730, 720, 690 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 1.03 (s, 3 H, CH_3), 1.14 (s, 3 H, CH_3), 1.30 (t, *J* = 7.2 Hz, 3 H, CH_2CH_3), 1.90–1.98 (m, 2 H), 2.07–2.13 (m, 2 H), 2.23 (t, *J* = 7.7 Hz, 2 H), 2.25–2.28 (m, 1 H), 3.03 (dt, *J* = 17.4, 7.2 Hz, 1 H, CHaC=O), 3.26 (dt, *J* = 17.4, 7.7 Hz, 1 H, CHbC=O), 4.17–4.22 (m, 2 H, OCH_2), 7.42–7.47 (m, 2 H, ArH), 7.51–7.54 (m, 1 H, ArH), 7.97–8.00 (m, 2 H, ArH).

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 14.0 (CH_3), 15.6 (CH_3), 24.0 (CH_2), 27.8 (CH_3), 33.7 (CH_2), 36.1 (CH_2), 36.7 (CH_2), 51.7 (CH), 60.5 (OCH_2), 72.9 (C-2), 127.9 (Ar_{CH}), 128.1 (Ar_{CH}), 132.5 (Ar_{CH}), 137.1 (Ar_C), 175.4 (OC=O), 200.0 (Ph*C*=O).

MS (EI): *m*/*z* = 315 (M, 1%).

Anal. Calcd for $C_{19}H_{25}NO_3 \cdot 0.5H_2O$: C, 70.3; H, 7.8; N, 4.3. Found: C, 70.1; H, 8.2; N, 4.0.

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