Tetrahedron 64 (2008) 11908–11916

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

# Dioxime oxalates; new iminyl radical precursors for syntheses of *N*-heterocycles

Fernando Portela-Cubillo [a], James Lymer [a], Eoin M. Scanlan [a,†], Jackie S. Scott [b], John C. Walton [a,*]

[a] University of St. Andrews, School of Chemistry, EaStChem, St. Andrews, Fife, KY16 9ST, UK
[b] GlaxoSmithKline, New Frontiers Science Park, Third Avenue, Harlow, Essex, CM19 5AW, UK

ARTICLE INFO

*Article history:*
Received 1 July 2008
Accepted 1 August 2008
Available online 20 September 2008

*Keywords:*
Oximes
Dihydropyrroles
Phenanthridines
Radical cyclization

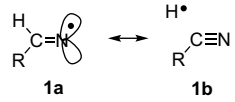
ABSTRACT

Symmetrical and unsymmetrical dioxime oxalates were prepared by treatment of oximes with oxalyl chloride. UV photolysis of these precursors was found to be an atom-efficient way of generating iminyl radicals. The process was most efficient for dioxime oxalates having aryl substituents attached to their C=N bonds. The method was useful for EPR spectroscopic study of iminyl and iminoxyl radicals. Photolyses in toluene solution, of dioxime oxalates containing alkenyl acceptor groups, yielded unsaturated iminyl radicals that ring closed to afford 3,4-dihydro-2*H*-pyrroles in good yields. Dioxime oxalates with biphenyl substituents also released iminyl radicals that ring closed onto the aromatic acceptor groups and, in acetonitrile solution, this approach provided a useful and atom-efficient method of making substituted phenanthridines.



## 1. Introduction

New preparative methods that are more environmentally friendly, and that allow access to new ranges of *N*-heterocycles, are emerging from *N*-centered radical reactions.[1,2] Of the available radical types, iminyls rank high because a wide variety can be generated that react rapidly in C–N bond forming processes. For EPR spectroscopic studies, alkyliminyl radicals have been generated by addition of electrons to nitriles followed by protonation (or by addition of H-atoms to nitriles),[3] by thermal rearrangements of oxime thionocarbamates,[4] and by H-atom abstraction from imines.[5] Both alkyl- and aryliminyls have *g*-factors of about 2.0033, *a*(N) values close to 10 G and *a*(β-H) values of about 80 G. This, and other evidence, indicates that iminyls are σ-type species with their unpaired electrons in orbitals on the N-atoms *in the nodal plane* of the C=N π-system as shown in **1a**. The large *a*(β-H) values show that monoalkyliminyls are subject to hyperconjugation **1b**. The structure **1a** precludes substantial delocalization of the unpaired electron into the ring π-system of aryliminyls. Consequently, substituent effects on the reactivity of iminyls are weak-inductive and steric; strong effects from ring substituents of aryliminyls are not expected to come into play. These factors also imply that N–X bonds in $R_2C{=}N{-}X$ compounds will be weak compared to N–X bonds in other *N*-containing compounds. Recent determinations of the N–O BDEs of oximes [34.9 and 35.8 kcal mol$^{-1}$ for $Ph_2CN{-}OH$ and $Me_2CN{-}OH$, respectively] and N–H BDEs of imines [91.7 and 90.2 kcal mol$^{-1}$ for $Ph_2CN{-}H$ and $Me_2CN{-}H$, respectively][6] have supported these deductions. The data suggest iminyl radicals should form relatively easily from a variety of nitrogenous compounds (Scheme 1).




**Scheme 1.** Structure of iminyl radicals.

The first effort to incorporate iminyl radicals in synthetic processes was probably that of Forrester et al. who explored several methods, making most use of the persulfate oxidation of iminooxyacetic acids in water or aqueous acetonitrile. They used this approach to prepare azines,[7] phenanthridines,[8] pyridines,[9] heterocyclic analogs of α-tetralone and other derivatives.[10] This research initiated spiraling interest by synthetic chemists in iminyl radical mediated preparations. Iminyl radical precursors used with tin hydrides or transition metals, e.g., *N*-alkenyl-*S*-arylthiohydroxylamines,[11] *N*-benzotriazolylimines,[12] and oxime esters[11,13] are not ideal because of the toxicity of the metals. Organostannanes have also been used to generate vinyl radicals, which yield iminyl radicals by ring closure onto nitriles. A range of anticancer alkaloids including camptothecin, mappicine and luotonin A were synthesized via this methodology.[14] Direct or sensitized photolyses of oxime esters of *N*-hydroxypyridine-2-thione,[15] of ketoxime xanthates,[16] of acyloximes[17,18] and of *O*-(4-cyanophenyl)oximes[19] have also been used for iminyl radical mediated syntheses of heterocycles.

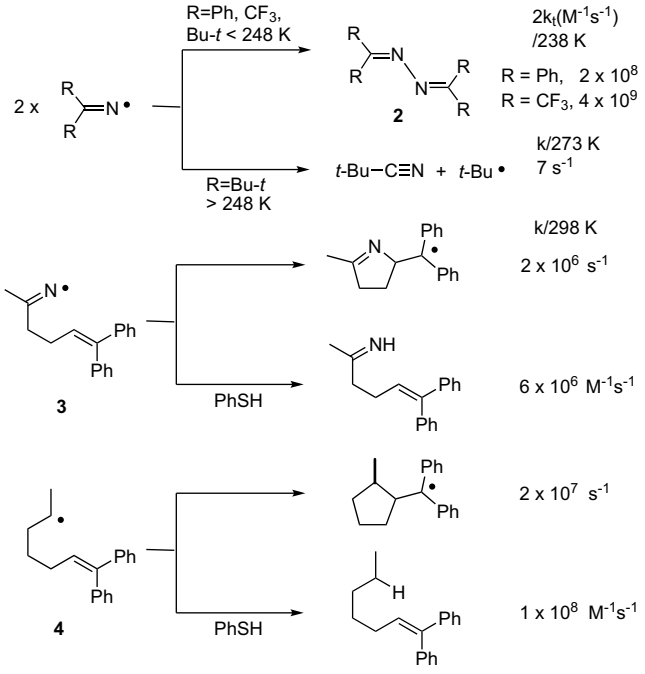
Thermal methods are usually advantageous in synthetic procedures. A few precursors suitable for thermal release of iminyls are

* Corresponding author. Tel.: +44 01334 463864; fax: +44 01334 463808.
*E-mail address:* jcw@st-and.ac.uk (J.C. Walton).
† Present address: School of Chemistry, University of Dublin, Trinity College, Dublin 2, Ireland.

0040-4020/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2008.08.112

known. Thus, quinolines and other heterocyclic derivatives were prepared by heating suitably functionalised *O*-2,4-dinitrophenyloximes with sodium hydride in dioxane.[20] Imidoyl radicals can be generated by radical addition to isonitriles. A subsequent cyclization onto a nitrile group then affords iminyl radicals. This sequence has been exploited in some elegant cascades resulting in cyclopenta-fused quinoxalines.[21] A direct thermal route, with promise of good flexibility, used thermal treatment of *O*-phenyl oxime ethers.[6] Iminyl radicals were smoothly released from these precursors by microwave irradiation and this method proved successful for preparations of dihydropyrroles, pyridoindoles and other heterocycles.[22]

In the absence of other reaction channels, iminyl radicals terminate by N–N coupling to give azines **2**. The large magnitudes of the rate constants of these dimerization reactions ($2k_t$) for small to moderately sized species (Scheme 2)[5] indicate that their coupling is diffusion controlled, just like the terminations of simple alkyl radicals. As expected, steric hindrance drastically reduces $2k_t$ for di-*tert*-butyliminyl, which undergoes slow dimerization ($2k_t = 4\times10^2$ $M^{-1}$ $s^{-1}$ at 238 K) at temperatures below 248 K, but β-scission above this (Scheme 2). However, β-scission reactions yielding nitriles are not important at $T$<ca. 420 K for aryliminyls or for iminyls with *primary*-alkyl substituents. H-atom abstraction by iminyl radicals yields imines. The rate constant for H-abstraction from thiophenol by model 6,6-diphenylhex-5-en-2-iminyl **3** was about a factor of 16 slower than the *C*-centered analog **4**.[23] 5-*exo*-Ring closure is very important from a synthetic perspective. The only available rate constant is again for iminyl **3** and measurement showed it to be a factor of 10 slower than *C*-centered model **4**. In a preparative sequence, ring closure is often in competition with H-abstraction by the iminyl intermediate. The fact that H-abstraction by iminyls is also comparatively slow is crucial for the success of many heterocycle syntheses.




**Scheme 2.** Rate constants for iminyl radical reactions (data from Refs. 5 and 23).

We knew from in-house work that oxime oxalate amides [$R_2C{=}NOC(O)C(O)NR'_2$] were good precursors for iminyl and carbamoyl radicals.[24] On sensitized photolysis benzaldehyde *O*-(aminooxalyl)oximes [$PhC(H){=}C(O)C(O)NR'_2$] yielded phenyliminyl radicals together with carbamoyl radicals. The latter radicals were useful for mediating syntheses of pyrrolidinones and azetidinones with benzaldehyde as the only by-product.

It seemed possible that dioxime oxalates **5** could function as particularly clean and atom-efficient sources of iminyl radicals; the only by-product being $CO_2$:

$R_2C{=}NOC(O)C(O)ON{=}CR_2 \rightarrow 2R_2C{=}N^{\bullet} + 2CO_2$;
**5**, **a** : R = Me, **b** : R = Ph

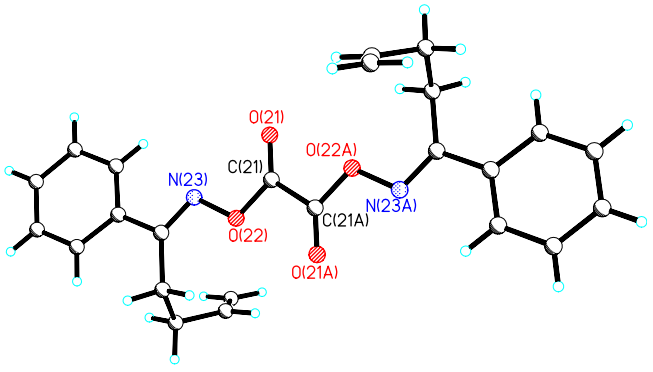
The only previous attempt to generate radicals from dioxime oxalates was briefly mentioned in a couple of reports from Forrester et al.[7,10] They concluded from EPR spectroscopic work and product analyses that both iminyl and iminoxyl radicals [$R_2C{=}NO^{\bullet}$] were formed during UV photolyses of **5**. In this paper we report our study of the preparation and photochemical reactions of a range of symmetrical and unsymmetrical dioxime oxalates. We show that they are useful iminyl radical precursors and can be adapted for syntheses of several types of heterocycles. Part of this research has previously been published as a preliminary communication.[25]

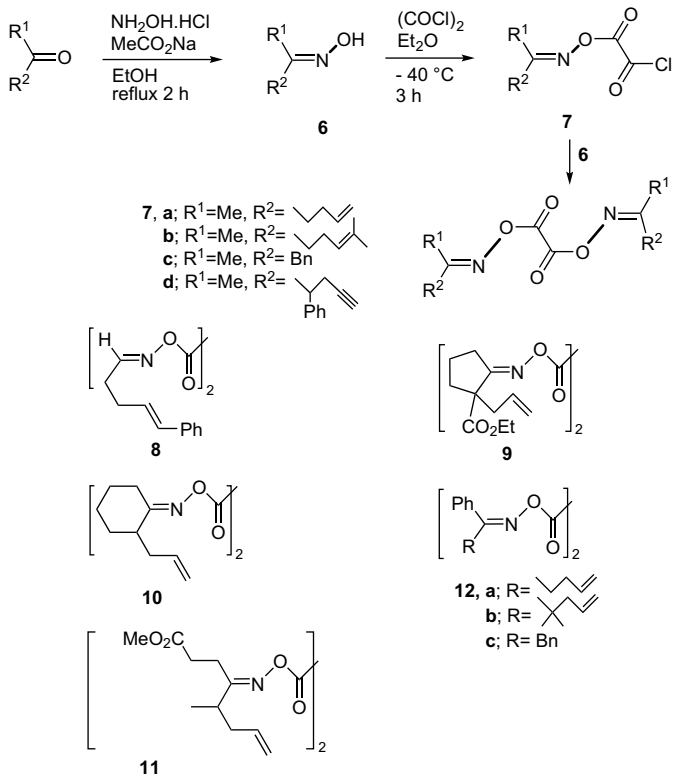
## 2. Results and discussion

### 2.1. Preparation of dioxime oxalates

Jochims and co-workers' synthetic strategy for dioxime oxalates involved condensation of an oxime with oxalyl chloride to give an oxime oxalyl chloride, which was then reacted with a second mole of oxime, in one pot, to afford the dioxime oxalate in good yield.[26] We used this method to prepare both symmetrical and unsymmetrical dioxime oxalates. Purification was usually impracticable because most dioxime oxalates were oils that hydrolyzed rapidly on exposure to air and during chromatography ($SiO_2$ or $Al_2O_3$) to give oxime and ketone. However, by using fresh oxalyl chloride, and by careful control of the reactant quantities, almost pure dioxime oxalates could be made quantitatively and used immediately without further purification. In a few cases solid dioxime oxalates resulted, which were purified by low temperature recrystallization. Most of the dioxime oxalates were obtained as mixtures of *E*/*Z* stereoisomers about their C=N bonds (Scheme 3).[27]

Dioxime oxalate **12a** was purified by crystallization from hexane at −20 °C and an X-ray crystal structure was obtained. Several data collections were attempted on this compound; the best solution is presented in Figure 1. We have not succeeded in obtaining X-ray data for any other dioxime oxalates, despite many attempts. The compound had *E* configurations about its C=N bonds and an extended all *trans*, all planar, arrangement of the central C=NOC(O)C(O)N=C unit. The observed N–O bond lengths (1.441(9) and 1.451(9) Å from two independent molecules within the unit cell) were slightly longer than those of oximes (1.38–1.43 Å)[28] suggesting they may be weaker and readily undergo homolysis.






**Scheme 3.** Symmetrical dioxime oxalates prepared.

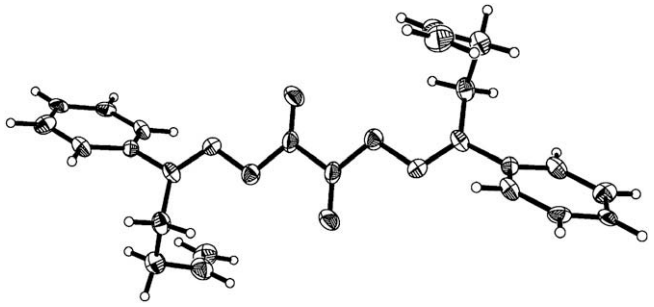


**Figure 1.** X-ray crystal structure of dioxime oxalate **12a**.

## 2.2. EPR spectroscopy of dioxime oxalates

Photochemical dissociations of **5a**,**b** and **7**–**11** were studied by 9 GHz EPR spectroscopy. Deaerated solutions of each dioxime oxalate in *tert*-butylbenzene were photolyzed with unfiltered light from a 500 W Hg lamp directly in the EPR resonant cavity. Signals were weak unless 4-methoxyacetophenone (MAP, 1 or 2 equiv) was included as photosensitizer. In that case good spectra were usually obtained. For example, **5a** and **5b** gave spectra of dimethyl- and diphenyl-iminyl radicals [$Me_2C{=}N^{\bullet}$ and $Ph_2C{=}N^{\bullet}$], respectively, with EPR parameters identical to those reported in the literature.[29]

Dioxime oxalates **7a**–**d** were examined in the same way and good EPR spectra of iminyl radicals were obtained from **7c** [Fig. 2(a); $g$=2.003, $a$(N)=9.8, $a$(3H)=1.3 G, at 240 K] and from **7d** [$g$=2.003, $a$(N)=9.8 G, $a$(3H)=1.2 G at 250 K]. Similarly, good spectra of the corresponding iminyl radicals were obtained from **12a**–**c** [Fig. 2(b) shows that from **12c**; $g$=2.003, $a$(N)=10.1 G at 280 K]. If the slightest trace of starting oxime was present, the iminyl radical spectrum was accompanied by that of the iminoxyl radical (Fig. 2(c)). However, iminoxyls were not observed when completely pure dioxime oxalates were employed. We believe,

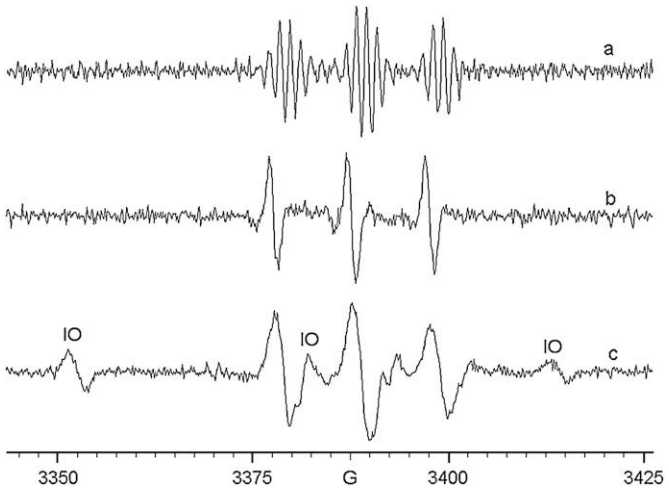



**Figure 2.** (a) EPR spectrum of iminyl radical from **7c** at 240 K. (b) EPR spectrum of iminyl radical from **12c** at 280 K. (c) EPR spectrum from **12c** containing a trace of oxime; the iminoxyl radical is indicated by IO.

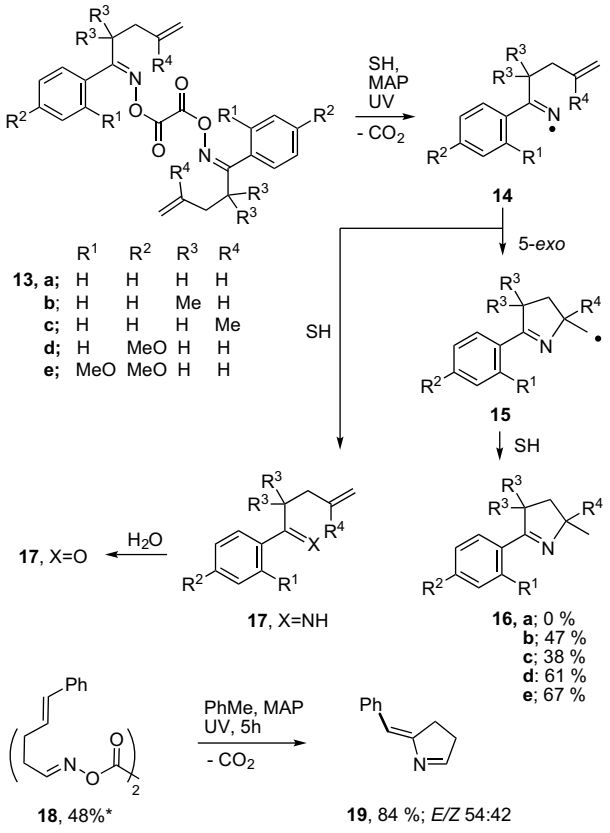
therefore, that the iminoxyl spectra result from H-atom abstraction, probably by MAP triplet states, from traces of oxime impurities and are not due to UV induced scission of the O–C bonds in dioxime oxalates. Iminoxyl radicals are persistent and have much longer lifetimes than iminyls so their concentration can build up to levels detectable by EPR spectroscopy even when only minute traces of $R_2C{=}NOH$ are present. The observation of iminoxyls by Forrester et al. was probably due to the same cause. No iminyl radicals were detected on spectral examination of any of the other dioxime oxalates, although iminoxyl radicals were detected in several cases, probably because of trace oxime impurities. We conclude that iminyl radical generation takes place much more readily when the dioxime oxalate contains an aromatic ring attached to, or close to, the C=N moiety of the dioxime oxalate. The presence of an aryl ring appeared to enhance energy pick-up by the dioxime oxalate from the MAP excited state.

## 2.3. Preparations of dihydropyrroles

5-*exo*-*trig* Ring closures of iminyl radicals containing pent-4-enyl substituents yield dihydropyrrole rings. To test the efficiency of this process for preparative purposes the set of dioxime oxalates **13a**–**e** shown in Scheme 4, each containing an aromatic ring adjacent to its C=N bond, was prepared. The expected mechanism is outlined in Scheme 4. By analogy with mono-oxime esters, the weak N–O bond of the dioxime oxalates should break first yielding iminyl radicals **14** and acyloxyl radicals. Rapid dissociation of the latter is expected to release a second iminyl radical along with two $CO_2$ molecules. The iminyl radicals **14** can then undergo ring closure in the favored 5-*exo*-*trig* mode to afford dihydropyrrolomethyl radicals **14** that abstract a hydrogen atom from the solvent (SH) with production of the 3,4-dihydro-2*H*-pyrroles **16**. Alternatively, iminyls **14** could directly abstract an H-atom from solvent with production of imines **17a**. The latter will readily hydrolyze to the corresponding ketones **17b**.

To find the optimum conditions, dioxime oxalate **13b** was reacted under various conditions and the product yields monitored (Table 1). The dioxime oxalate was dissolved in the solvent along with MAP and the solutions were photolyzed in quartz tubes with light from a 400 W medium pressure Hg lamp.

These results indicated that isopropanol and cyclohexa-1,4-diene were too efficient as H-atom donors, such that cyclization could not compete with reduction of the iminyl radical to imine. Toluene and cyclohexane were both satisfactory in this respect. The poor




**Scheme 4.** Formation of dihydropyrroles from UV photolyses of dioxime oxalates.

**Table 1**
Sensitized photolyses of dioxime oxalate **13b**[a]

| Solvent SH | Photolysis time/h | Temp/°C | Dihydropyrrole **16** (%) | Imine+ketone **17** (%) |
|---|---|---|---|---|
| Isopropanol | 6 | rt | 0 | 75 |
| CHD[b] | 6 | rt | 0 | 58 |
| Toluene | 8 | 85 | 31 | 24 |
| Toluene[c] | 4 | rt | 47 | 0 |
| Cyclohexane | 8 | 85 | 35 | 0 |

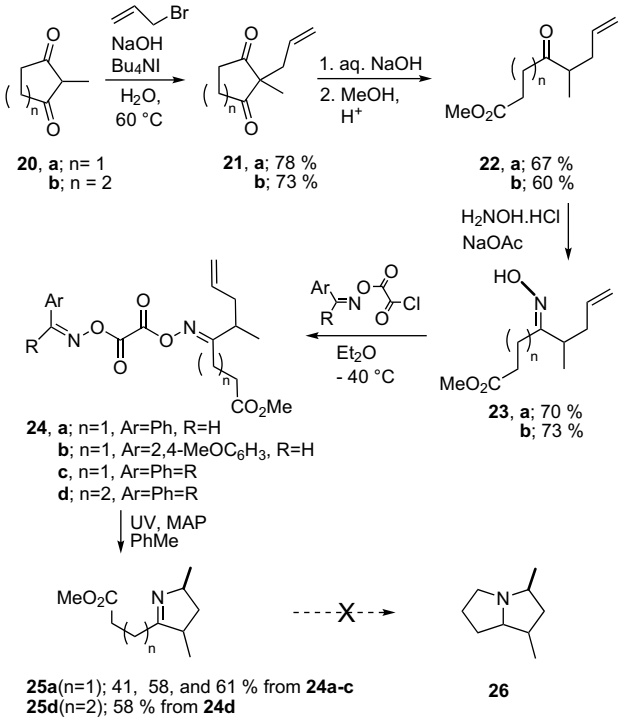
[a] MAP (1 equiv) included.
[b] CHD=cyclohexa-1,4-diene.
[c] MAP (2 equiv).

yields in the two experiments carried out at 85 °C suggested the dioxime oxalate degraded too rapidly at this temperature. The best combination was toluene solvent at rt with 2 equiv of MAP.

The optimum conditions developed with **13b** were applied to reactions of the rest of the set. After removal of MAP by chromatography the 5-aryl-3,4-dihydropyrroles **16b–e** were isolated in the yields shown in Scheme 4. We were unable to isolate any of **16a** partly because of its volatility. The yield of **16c** was lower, in agreement with the expected slower ring closure at the more substituted –CMe═ atom. The yield of **16b** was also comparatively low, i.e., no support was forthcoming for *gem* dimethyl enhancement of aryliminyl cyclization.

An interesting contrast was provided by dioxime oxalate **18** obtained from 5-phenylpent-4-en-1-al. After photolysis under similar conditions, the product isolated was 2-benzylidene-3,4-dihydro-2*H*-pyrrole **19**, instead of the expected benzyldihydropyrrole. In this case cyclization of the intermediate iminyl radical will afford a resonance-stabilized benzyl type radical for which H-atom abstraction from solvent will be much slower. Instead, the pyrrolobenzyl radical loses an H-atom to produce **9**. Possibly the mechanism involves electron transfer from the pyrrolobenzyl radical to MAP with production of the pyrrolobenzyl cation which then transfers a proton (see below).

Dihydropyrroles of type **25** were of interest because they can serve as precursors for biologically active pyrrolizidines and indolizidines.[30] The keto-esters **22** needed for the making suitable dioxime oxalate precursors were prepared by allylation of 2-methylcycloalkane-1,3-diones **20** as shown in Scheme 5.[31] The allylated cycloakanones **21** were ring opened and esterified yielding **22**, which were converted to the corresponding oximes in the standard way. A symmetrical dioxime oxalate was first prepared from **23a** and photolyzed in toluene. However, no dihydropyrrole was obtained on photolysis. Instead, the starting material and its hydrolysis products were recovered. The symmetrical dioxime oxalate contains no aryl ring and, in agreement with the conclusion mentioned above, iminyl generation was much less efficient.



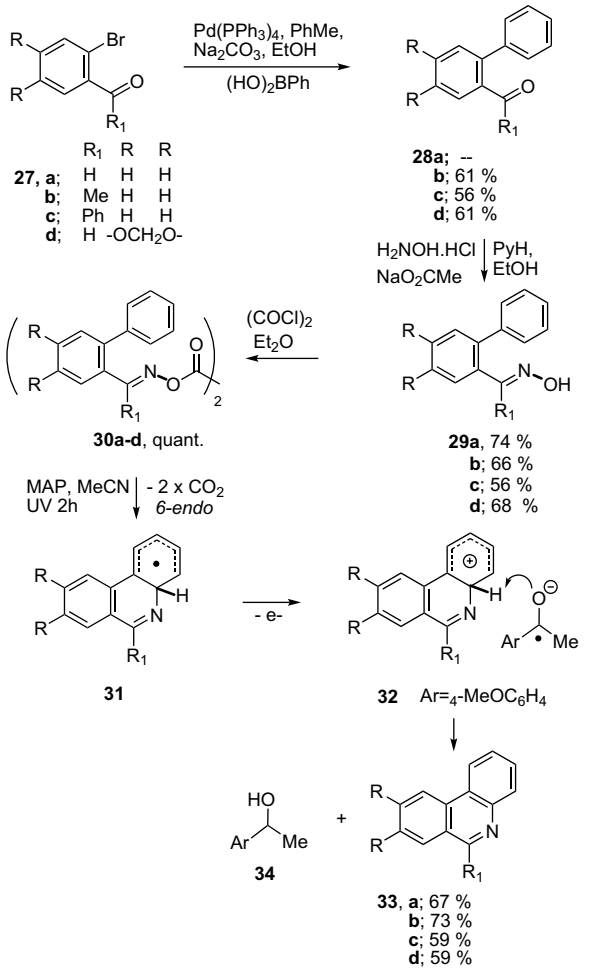

**Scheme 5.** Preparation of methyl (3,4-dihydro-2*H*-pyrrol-5-yl)alkanoates.

To overcome this problem unsymmetrical dioxime oxalates **24a–d**, with one half containing an aromatic oxime, were examined. They were prepared by reacting the oxime oxalyl chlorides from benzaldehyde, 2,4-dimethoxybenzaldehyde or benzophenone with the ester oximes **23**. Photolyses of these precursors with MAP did indeed afford dihydropyrroles **25** along with the arylimines (plus ketones from hydrolysis) produced by hydrogen transfer to the aryl-iminyl radicals. The somewhat greater yields of **25a** from **24b–d** (Scheme 5) suggested there was an advantage in using dimethoxy-substitution of the aromatic part or in employing benzophenone. It can be concluded that dihydropyrroles like **25**, with no aryl substituents, can be made in good yields by employing unsymmetrical dioxime oxalates but, of course, this reduces the atom-efficiency of the method.

We investigated methods for converting ester-containing dihydropyrrole **25a** into a pyrrolizidine derivative **26** by means of an intramolecular nucleophilic substitution. Complete reduction of the imine and ester was therefore carried out with $LiAlH_4$. An Appel type method, which has worked for other pyrrolizidine derivatives,[30] was tried. However, when the amine was treated with $PPh_3$, $CCl_4$ and $Et_3N$ in DCM only intractable mixtures were obtained.

## 2.4. Preparation of phenanthridines

Judging by literature precedent, iminyl radicals can also ring close onto aromatic acceptors, in appropriate circumstances. To broaden the scope of our methodology we prepared dioxime oxalates **30a–d** as shown in Scheme 6. The biphenyl derivatives **28a–d** were obtained in good yields by Suzuki coupling of the aromatic carbonyl compounds **27a–d** with phenyl boronic acid. The oximes **29a–d** were obtained by the standard method and converted to symmetrical dioxime oxalates **30a–d** essentially quantitatively.




**Scheme 6.** Preparation of phenanthridines via dioxime oxalates.

In this case, it was expected that the iminyl radicals released on photolyses of **30** would preferentially undergo 6-*endo* cyclization onto the phenyl acceptors because this would yield the resonance-stabilized cyclohexadienyl type radicals **31**. The latter are too thermodynamically stabilized to abstract H-atoms from the solvent. Instead, they should re-aromatize and afford phenanthridines **33** (Scheme 6). To find the best conditions for achieving this outcome, dioxime oxalate **30a** was photolyzed at rt in several different solvents and under various conditions as shown in Table 2.

Heterocycle formation proceeded satisfactorily in the absence of photosensitizer (entries 1 and 2) but a better yield was obtained by inclusion of 2 equiv of MAP (entry 3). Comparison of entries 3 and 4 indicated that 2 h irradiation was more efficient than 4 h irradiation. Entry 6 shows that *tert*-butanol was not satisfactory as a solvent. Although a good yield was obtained in *t*-BuPh (entry 5), acetonitrile was more convenient to use, so the conditions of entry 3 were adopted as standard. Using these conditions the

**Table 2**
Yields of phenanthridine (**33a**) from UV photolysis of **30a** at rt

| Entry | Solvent | MAP[a]/equiv | Photolysis time/h | Yield of **33a** /mol %[b] |
|---|---|---|---|---|
| 1 | $CH_3CN$ | None | 2 | 42 |
| 2 | $CH_3CN$ | None | 4 | 66 |
| 3 | $CH_3CN$ | 2 | 2 | 76 [67][c] |
| 4 | $CH_3CN$ | 2 | 4 | 71 |
| 5 | *t*-BuPh | 2 | 2 | 69 |
| 6 | *t*-BuOH | 2 | 2 | 34 |

[a] 4-Methoxyacetophenone.
[b] Determined by NMR.
[c] Isolated yield.

phenanthridine derivatives **33a–c** were obtained in good yields (Scheme 6). The reaction was tolerant of Me and Ph substituents on the iminyl radical.

In a similar vein, the plant alkaloid trisphaeridine **33d** was prepared in four steps starting from commercial 6-bromopiperonal. A 59% yield of **33d** was obtained from UV irradiation of **30a** in acetonitrile. Previous syntheses have been accomplished via tributyltin hydride induced cyclization of *N*-(2-bromobenzyl)aniline,[32] via the internal Pd-catalyzed aryl–aryl coupling reaction of MOM protected halo amides, followed by reduction with $LiAlH_4$ and treatment with hydrochloric acid,[33] and by Pd[0]-mediated Ullmann cross-coupling of 1-bromo-2-nitrobenzene with 6-brom opiperonal.[34]

The mechanism of the final oxidation may involve electron transfer from the cyclohexadienyl radical **31** to MAP yielding the corresponding delocalized cation **32**, together with $MAP^{-\bullet}$ radical anion. Proton transfer from **32** to $MAP^{-\bullet}$ would then yield the phenanthridine **33** together with $MAPH^{\bullet}$, which would pick up hydrogen in solution to give 1-(4-methoxyphenyl)ethanol **34**. This alcohol was detected by NMR and MS in several reactions.

## 3. Conclusions

Dioxime oxalates are easily and efficiently prepared from a wide variety of oximes and can be used immediately without purification for UV generation of iminyl radicals. The process works best with precursors having aryl substituents attached to their C=N bonds. The advantage over other precursors is that the symmetrical variety cleanly release just one type of iminyl radical. The method is useful for EPR spectroscopic study of iminyl and iminoxyl radicals. Photolyses of dioxime oxalates containing alkenyl acceptor groups yield iminyl radicals that ring close to 3,4-dihydro-2*H*-pyrroles in toluene solution. Iminyl radicals also ring close onto aromatic acceptor groups and, in acetonitrile, the intermediate cyclohexadienyl type radicals aromatize. This approach provides a useful and atom-efficient method of making phenanthridines.

## 4. Experimental

### 4.1. General procedures

$^1H$ NMR spectra were recorded at 400 MHz using $CDCl_3$ solvent as reference and/or internal deuterium lock. $^{13}C$ NMR spectra were recorded at 75.5 MHz using the PENDANT sequence and internal deuterium lock. The chemical shifts for all NMR spectra are expressed in parts per million to high frequency of TMS reference. Coupling constants are quoted in hertz and are recorded to the nearest 0.1 Hz. The IR spectra were obtained with an FTIR system. Solids were run as Nujol mulls and liquids were run as thin films on NaCl plates. Low-resolution and high-resolution (HR) mass spectral analysis (CI) were recorded using either quadrupole or a time-of-flight orthogonal acceleration spectrometer coupled to a GC system. Electrospray mass spectra (ESMS) were recorded on a high

performance orthogonal acceleration reflecting TOF mass spectrometer coupled to an HPLC instrument. Only major peaks are reported and intensities are quoted as percentages of the base peak. TLC was carried out using silica plates (0.2 mm with 254 nm fluorescent dye) and the components were observed under UV light (254 nm/365 nm). Column chromatography was performed using silica gel (40–63 μm). Hexane, DCM, ethyl acetate, and toluene were used as-supplied. Pyridine was dried with KOH. Nitrogen gas was dried (NaOH, $CaCl_2$, 4 Å molecular sieves) prior to use.

Note that because of rapid hydrolysis and degradation it was not possible to obtain full characterizing data for any of the oxime oxalyl chlorides or for several of the dioxime oxalates.

### 4.2. EPR spectra

EPR spectra were obtained with a Bruker EMX 10/12 spectrometer operating at 9.5 GHz with 100 kHz modulation. Solutions of freshly prepared dioxime oxalate (ca. 0.1–0.2 M) and 4-methoxyacetophenone (MAP, usually 2 mol equiv) in *tert*-butylbenzene were placed in 4.0 mm o.d. quartz tubes and deaerated by bubbling nitrogen gas for 20 min. Samples were irradiated in the resonant cavity by unfiltered light from a 500 W super pressure Hg arc. In all cases where spectra were obtained, hfs were checked with the aid of computer simulations using the Bruker SimFonia software package. Microwave power 1.0 mW; modulation amplitude 0.2–1.0 $G_{pp}$.

### 4.3. Syntheses of precursors

*Hex-5-en-2-one oxime*[35] (**6a**), *6-methylhept-5-en-2-one oxime*[36] (**6b**), *phenylacetone oxime*[37] (**6c**), *3-phenylhex-5-yn-2-one oxime*[38] (**6d**), and *1-phenylpent-4-en-1-one oxime*[39] were prepared by literature procedures.

#### 4.3.1. *Hex-5-en-2-one dioxime oxalate (**7a**)*

Oxime **6a** (0.2 g, 1.77 mmol) in ether (3 mL) was added dropwise to a cold (−40 °C) solution of oxalyl chloride (0.34 g, 2.65 mmol) in ether (16 mL) and stirred for 1 h at −20 °C. More **6a** (0.4 g, 3.54 mmol) in ether (6 mL) was added dropwise to the cold reaction mixture (−40 °C) and stirred for a further 20 min at this temperature and 1 h at rt. Evaporation of solvent gave the crude product, which was purified by flash chromatography using alumina and ethyl acetate/hexane (1:9) as eluent; colorless liquid (0.86 g, 65%) containing a mixture of several isomers; $^1$H NMR, $\delta_H$ 5.8 (2H, m), 4.95–5.1 (4H, m), 2.45 (4H, s), 2.35 (4H, s), 2.1 (6H, s); $^{13}$C NMR, $\delta_C$ 168.7 (C, major isomer), 136.6 (CH, major isomer), 136.3 (CH, minor isomer), 116.7 (CH, minor isomer), 116.5 (CH, major isomer), 35.3 ($CH_2$, major isomer), 35.2 ($CH_2$, minor isomer), 30.7 ($CH_2$, minor isomer), 30.3 ($CH_2$, major isomer), 20.4 ($CH_3$, minor isomer), 16.3 ($CH_3$, major isomer); IR, $\nu_{max}$/cm$^{-1}$ 1784, 1761, 1642; *m*/*z* (%) (CI), 281 ($MH^+$, 12%); HRMS, $C_{14}H_{21}N_2O_4$ ($MH^+$) requires 281.1501; found 281.1512.

#### 4.3.2. *6-Methylhept-5-en-2-one dioxime oxalate (**7b**)*

Method as for **7a**; light yellow oil (99%), which contained a mixture of several isomers. $^1$H NMR, $\delta_H$ 5.1 (2H, m), 2.2–2.5 (8H, m), 2.1 (6H, m), 1.65 (6H, s), 1.7 (12H, s); $^{13}$C NMR, $\delta_C$ 169.1(C), 134.2 (C), 133.7 (C), 122.3 (CH), 122.2 (CH), 122.1 (CH), 121.9 (CH), 36.0 ($CH_2$), 35.9 ($CH_2$), 31.5 (2×$CH_2$), 26.0 ($CH_3$), 25.0 ($CH_2$), 24.8 ($CH_2$), 24.7 ($CH_2$), 20.5 ($CH_3$), 20.4 ($CH_3$), 18.1 ($CH_3$), 18.0 ($CH_3$), 16.3 ($CH_3$), 16.2 ($CH_3$); IR, $\nu_{max}$/cm$^{-1}$ 1787, 1763, 1648; *m*/*z* (%) (ES), 359 ($MNa^+$, 100%); HRMS, $C_{18}H_{28}N_2O_4Na$ requires 359.1947; found 359.1941.

#### 4.3.3. *Phenylacetone dioxime oxalate (**7c**)*

Method as for **7a**; colorless oil; mixture of three isomers (98%); $^1$H NMR, $\delta_H$ 7.2–7.4 (10H, m), 3.8 (4H, m), 3.62 (4H, m), 1.9 (6H, m); $^{13}$C NMR, $\delta_C$ 168.4 (C), 135.0 (C), 127.7–129.0 (CH), 42.0 ($CH_2$, 1 isomer), 41.9 ($CH_2$, 1 isomer), 37.6 ($CH_2$, 1 isomer), 20.3 ($CH_3$), 16.1 ($CH_3$), 16.0 ($CH_3$); IR, $\nu_{max}$/cm$^{-1}$ 1787, 1760, 1646, 1602; *m*/*z* (%) (ES), 375 ($MNa^+$, 30), 258 (100); HRMS, $C_{20}H_{20}N_2O_4Na$ ($MNa^+$) requires 375.1321; found 375.1328.

#### 4.3.4. *3-Phenylhex-5-yn-2-one dioxime oxalate (**7d**)*

Method as for **7a**; light red oil (96%); $^1$H NMR, $\delta_H$ 7.25–7.4 (5H, m), 3.87 (1H, t, *J* 7.7), 2.7–3.0 (2H, m), 1.97 (1H, t, *J* 2.6), 1.95 (3H, s); $^{13}$C NMR, $\delta_C$ 169.8 (C), 137.5 (C), 129.5 (CH), 128.61 (CH), 128.4 (CH), 81.3 (C), 71.01 (CH), 51.5 (CH), 22.3 ($CH_2$), 15.9 ($CH_3$); IR, $\nu_{max}$/cm$^{-1}$ 3297, 1786.

#### 4.3.5. *5-Phenylpent-4-enal dioxime oxalate (**8**)*

5-Phenylpent-4-enal oxime (0.42 g, 2.4 mmol) was dissolved in dry ether (5 mL) and added dropwise to a stirred solution of oxalyl chloride (0.15 g; 1.2 mmol) in ether (5 mL) at −40 °C. The mixture was stirred at −40 °C for 20 min and then allowed to stir at rt for 2 h. After this time the solvent was removed to give the dioxime as a yellow oil (0.49 g; 100%); $^1$H NMR, $\delta_H$ (300 MHz, $CDCl_3$) 2.50 (4H, m, 4×$CH_2$), 6.19 (2H, dt, $J_d$=15.9, *J* 6.7, 2×=CH), 6.53 (1H, d, *J* 15.9, 2×=CH), 7.25–7.40 (12H, m, PhH, 2×CHN); $^{13}$C NMR, $\delta_C$ 18.0 ($CH_2$), 29.2 (CH2), 125.8 (CH), 126.7 (2×CH), 128.1 (CH), 129.0 (2×CH), 133.3 (CH), 137.0 (C), 152.3 (C=N).

#### 4.3.6. *1-Allyl-2-oxocyclopentanone carboxylic acid ethyl ester dioxime oxalate (**9**)*

Method as for **7a**; colorless oil, mixture of isomers (96%); $^1$H NMR, $\delta_H$ 5.6–5.9 (2H, m), 5.1–5.2 (4H, m), 4.2 (4H, q, *J* 7.2), 2.58–2.85 (8H, m), 2.3–2.4 (2H, m), 1.82–1.88 (6H, m), 1.27 (6H, t, *J* 7.2); $^{13}$C NMR, $\delta_C$ 177.9 (C), 172.0 (C), 133.4 (CH, minor isomer), 133.0 (CH, major isomer), 120.0 ($CH_2$, major isomer), 119.9 ($CH_2$, minor isomer), 62.3 ($CH_2$, major isomer), 62.2 ($CH_2$, minor isomer), 58.2 (C), 39.7 ($CH_2$), 35.4 ($CH_2$), 30.7 ($CH_2$, major isomer), 30.4 ($CH_2$, minor isomer), 22.0 ($CH_2$), 14.5 ($CH_3$); IR, $\nu_{max}$/cm$^{-1}$ 1797, 1767, 1731, 1654, 1641.

#### 4.3.7. *2-Allylcyclohexanone dioxime oxalate (**10**)*

Method as for **7a**; red oil, which was purified by flash chromatography using alumina and eluting with petroleum ether/ethyl acetate (9:1) to give a clear viscous liquid (60%) containing several isomers; $^1$H NMR, $\delta_H$ 5.6–5.9 (2H, m), 5.0–5.1 (4H, m), 1.4–2.5 (22H, m); $^{13}$C NMR, $\delta_C$ 174.2 (C), 133.4–136.1(CH), 117.2–119.0 ($CH_2$), 42.5 (CH), 39.6–40.0 ($CH_2$), 35.4–36.4 ($CH_2$), 35.7 (CH), 32.1–32.6 ($CH_2$), 28.7–29.8 ($CH_2$), 26.2–26.9 ($CH_2$), 25.5–25.9 ($CH_2$), 23.3–24.4 ($CH_2$); IR, $\nu_{max}$/cm$^{-1}$ 1783, 1760, 1639; *m*/*z* (%) (ES), 383 ($MNa^+$, 100), 262 (25); HRMS, $C_{20}H_{28}N_2O_4Na$ requires: 383.1947; found 383.1938.

#### 4.3.8. *1-Phenylpent-4-en-1-one dioxime oxalate (**12a**)*

Method as for **7a**; colorless solid, which was recrystalised from DCM at 253 K to give colorless prisms (40%) containing several isomers; $^1$H NMR, $\delta_H$ 7.6–7.8 (4H, m), 7.35–7.5 (6H, m), 5.7–5.9 (2H, m), 4.9–5.1 (4H, m), 3.1 (4H, t, *J* 7.7), 2.35–2.4 (4H, m); $^{13}$C NMR, $\delta_C$ 169.7 (C), 136.4 (CH, major isomer), 136.2 (CH, minor isomer), 133.1 (C, major isomer), 132.6 (C, minor isomer), 127.5–132.0 (12×CH), 117.0 (CH, minor isomer), 116.6 (CH, minor isomer), 30.4–31.1 ($CH_2$), 28.2–28.7 ($CH_2$); IR, $\nu_{max}$/cm$^{-1}$ 1791, 1766, 1641, 1600; *m*/*z* (ES) 427 ($MNa^+$). X-ray data in the Supplementary data and in CCDC 696935.

#### 4.3.9. *Deoxybenzoin dioxime oxalate (**12c**)*

Method as for **7a**; cream oil (90%); $^1$H NMR, $\delta_H$ 7.7–7.8 (2H, m), 7.18–7.44 (8H, m), 4.3 (2H, s); $^{13}$C NMR, $\delta_C$ 168.0 (C), 160.6 (C), 134.6 (C), 132.9 (C), 132 (CH), 127.4–129.6 (8H, CH), 35.2 (CH); IR, $\nu_{max}$/cm$^{-1}$ 1785, 1684.

#### 4.3.10. 2,2-Dimethyl-1-phenylpent-4-en-1-one dioxime oxalate (**13b**)

White solid; 76%; $^1$H NMR (400 MHz, $CDCl_3$), $\delta_H$ 1.13 (12H, s, $CH_3$), 2.22 (4H, d, $J$=7.2 Hz, $CH_2$), 5.04 (4H, m, $CH_2$), 5.78 (2H, m, CH), 6.91–7.05 (4H, m, CH), 7.28–7.43 (6H, m, CH); $^{13}$C NMR, $\delta_C$ 25.9 ($CH_2\times2$), 41.9 (C×2), 44.2 ($CH_3\times4$), 118.6 ($CH_2\times2$), 126.7 (CH×4), 128.2 (CH×4), 128.8 (CH×2), 131.7 (C×2), 133.8 (CH×2), 163.3 (C×2), 173.8 (C×2); IR, $\nu_{max}$/cm$^{-1}$ 1675, 1591. HRMS (ES), $C_{28}H_{32}N_2O_4Na$; requires 483.2260; found: 483.2267.

#### 4.3.11. 4-Methyl-1-phenylpent-4-en-1-one dioxime oxalate (**13c**)

Red oil; $^1$H NMR (400 MHz, $CDCl_3$), $\delta_H$ 1.66–1.70 (6H, s, $CH_3$), 2.15 (4H, t, $J$=7.9 Hz, $CH_2$), 2.94–2.96 (4H, m, $CH_2$), 4.60 (2H, m, $CH_2$), 4.66 (2H, m, $CH_2$), 7.28–7.44 (6H, m, CH), 7.54–7.61 (4H, m, CH); $^{13}$C NMR, $\delta_C$ 22.2 ($CH_3$)×2, 26.9 ($CH_2$)×2, 34.4 ($CH_2$)×2, 111.1 ($CH_2$)×2, 127.3 (CH)×4, 128.9 (CH)×4, 131.2 (CH)×2, 133.0 (C)×2, 144.1 (C)×2, 157.1 (C)×2, 167.8 (C)×2; IR, $\nu_{max}$/cm$^{-1}$ 1786, 1760, 1653, 1590, 1443.

#### 4.3.12. 1-(4-Methoxyphenyl)pent-4-en-1-one dioxime oxalate (**13d**)

Red oil; $^1$H NMR (400 MHz, $CDCl_3$), $\delta_H$ 2.23 (4H, m, $CH_2$), 2.88 (4H, t, $J$=7.7 Hz, $CH_2$), 3.74 (6H, s, $CH_3$), 4.94 (4H, m, $CH_2$), 5.68 (2H, m, CH), 6.82 (4H, d, $J$=8.6 Hz, CH), 7.55 (4H, d, $J$=8.6 Hz, CH); $^{13}$C NMR, $\delta_C$ 27.5 ($CH_2$)×2, 30.9 ($CH_2$)×2, 55.5 ($CH_3$)×2, 114.2 (CH)×4, 116.2 ($CH_2$)×2, 125.0 (C)×2, 129.1 (CH)×4, 136.2 (CH)×2, 160.9 (C)×2, 162.2 (C)×2, 166.5 (C)×2; IR, $\nu_{max}$/cm$^{-1}$ 1768, 1723, 1605.

#### 4.3.13. 1-(2,4-Dimethoxyphenyl)pent-4-en-1-one dioxime oxalate (**13e**)

$^1$H NMR (400 MHz, $CDCl_3$), $\delta_H$ 2.06–2.70 (8H, m, $CH_2$), 3.71–3.81 (12H, m, $CH_3$), 4.97 (4H, m, $CH_2$), 5.77 (2H, m, CH), 6.43 (4H, m, CH), 7.51 (1H, m, CH), 8.16 (1H, m, CH); $^{13}$C NMR, $\delta_C$ 27.8/29.6/30.1 ($CH_2$)×2, 34.4/34.5/37.0 ($CH_2$)×2, 55.8 ($CH_3$)×4, 98.6/98.7/99.8 (CH)×2, 103.7/104.6/105.2 (CH×2), 115.7 ($CH_2$)×2, 120.7/129.6/130.5 (CH)×2, 121.4 (C)×2, 149.1 (C)×2, 156.3 (C)×2, 161.9 (C)×2, 169.9/174.6 (C)×2; IR, $\nu_{max}$/cm$^{-1}$ 1768, 1705, 1605, 1512.

#### 4.3.14. Photolysis of 1-phenylpent-4-en-1-one dioxime oxalate (**13a**)

Dioxime oxalate **13a** (0.52 g, 1.29 mmol) and MAP (1 equiv) were dissolved in ether (450 mL) and the mixture was photolyzed for 5 h at rt. The alcohol **34**; $\delta_H$ 7.30 (2H, d, $J$ 8.5), 6.83 (2H, d, $J$ 8.7), 4.86 (1H, q, $J$ 6.4), 3.8 (3H, s), 1.48 (3H, d, $J$ 6.6); $m/z$ (%) 152 (2), 134 (100), 135 (100), and imine **17a**, $m/z$: 159 (100), 104 (80) were identified in the product mixture. An attempt was made to isolate these components via column chromatography using silica and eluting with EtOAc/pet ether (5% EtOAc to pure EtOAc) but no dihydropyrrole structure could be identified from the $^1$H NMR spectra. A repeat of the reaction where the photolysis was for 8 h at rt gave the same components as before. Photolyses were also carried out in 1,4-cyclohexadiene, 2-propanol, and toluene but no dihydropyrrole was isolated.

#### 4.3.15. Photolysis of 2,2-dimethyl-1-phenylpent-4-en-1-one dioxime oxalate (**13b**)

Compound **13b** (24.3 mg, 0.053 mmol) and MAP (1 equiv) were dissolved in cyclohexane (2 mL) and the mixture was photolyzed for 8 h at 85 °C. Chromatography yielded 3,4-dihydro-2,4,4-trimethyl-5-phenyl-2*H*-pyrrole **16b** (35%), $^1$H NMR, $\delta_H$ 7.64–7.7 (2H, m), 7.14–7.4 (3H, m), 4.10 (1H, dp, $J$ 6.7, 8.4), 2.11 (2H, dd, $J$ 6.7, 12.5), 1.39 (3H, d, $J$ 6.9), 1.35 (6H, s); $^{13}$C NMR, $\delta_C$ 129.8 (C), 128.5 (CH), 128.3 (CH), 63.7 (CH), 50.4 (C), 27.9 ($CH_3$), 27.1 ($CH_2$), 26.3 ($CH_3$), 22.6 ($CH_3$); $m/z$ (%) 187 (100), 131 (60), 84 (80); HRMS, $C_{13}H_{18}N$ ($MH^+$) requires 188.1439; found 188.1432. Similar photolyses in toluene, cyclohexa-1,4-diene, 2-propanol, and diethyl ether gave **16b** together with imine **17a** and ketone **17b** in the yields recorded in Table 1.

#### 4.3.16. 5-(4-Methoxyphenyl)-2-methyl-3,4-dihydro-2H-pyrrole (**16d**)

Red oil; 61%; $^1$H NMR (400 MHz, $CDCl_3$), $\delta_H$ 1.28 (3H, d, $J$=6.8, $CH_3$), 1.46 (1H, m, $CH_2$), 2.15 (1H, m, $CH_2$), 2.78 (1H, m, $CH_2$), 2.96 (1H, m, $CH_2$), 3.78 (3H, s, $CH_3$), 4.20 (1H, m, CH), 6.83 (2H, d, $J$=8.8 Hz, CH), 7.71 (2H, d, $J$=8.8 Hz, CH); $^{13}$C NMR, $\delta_C$ 22.2 ($CH_3$), 30.7, 35.2 ($CH_2$), 55.6 ($CH_3$), 68.2 (CH), 113.8 (CH×2), 127.4 (C), 129.3 (CH×2), 161.2, 171.1 (C); IR, $\nu_{max}$/cm$^{-1}$ 3268, 2923, 1684; HRMS (CI), $C_{12}H_{16}NO$ requires 190.1232; found 190.1238.

#### 4.3.17. 5-(2,4-Dimethoxyphenyl)-2-methyl-3,4-dihydro-2H-pyrrole (**16e**)

A solution of the dioxime oxalate (400 mg, 0.57 mmol) and MAP (171 mg, 1.14 mmol) in toluene (25 mL) was photolyzed for 4 h at rt by light from a 400 W UV lamp. After this time the toluene was evaporated to dryness to give a yellow oil. The oil was purified by column chromatography (10% EtOAc/hexane); red oil; 67%; $^1$H NMR (400 MHz, $CDCl_3$), $\delta_H$ 1.28 (3H, d, $J$=6.7 Hz, $CH_3$), 1.44 (1H, m, $CH_2$), 2.12 (1H, m, $CH_2$), 2.88 (1H, m, $CH_2$), 3.04 (1H, m, $CH_2$), 3.77 (3H, s, $CH_3$), 3.78 (3H, s, $CH_3$), 4.12 (1H, m, CH), 6.43 (2H, m, CH), 7.68 (1H, d, $J$=8.5, CH); $^{13}$C NMR, $\delta_C$ 21.9 ($CH_3$), 30.1, 38.1 ($CH_2$), 55.5 ($CH_3\times2$), 66.4 (CH), 98.6, 105.1 (CH), 116.6 (C), 131.7 (CH), 159.0, 165.8, 172.3 (C); IR, $\nu_{max}$/cm$^{-1}$ 3018, 2964, 1609; HRMS (CI), $C_{13}H_{18}NO_2$ requires 220.1338; found: 220.1337.

#### 4.3.18. Benzylidene-3,4-dihydro(2H)pyrrole (**19**)

From photolysis (5 h, rt) of **18** (500 mg; 3.6 mmol) and MAP (540 mg, 3.6 mmol) in toluene (400 mL); yellow oil (84%). $^1$H NMR and GC–MS showed this to be a mixture of two isomers; $^1$H NMR (300 MHz, $CDCl_3$), $\delta_H$ 2.45–2.75 (4H, m, $2\times CH_2$), 5.57 (1/2H, dt, $J$ 13.2, $J$ 6.5, C=CHPh), 6.11 (1/2H, dt, $J$ 15.9, $J$ 4.9, C=CHPh), 6.44 (1/2H, d, $J$ 15.9), 6.52 (1/2H, d, $J$ 13.2, HC=N), 7.25–7.40 (5H, m, PhH); $\delta_C$ 18.0 ($2\times CH_2$), 24.8 ($CH_2$), 29.2 ($CH_2$), 125.9, 126.7, 127.6, 127.9, 128.1, 128.8, 129.0 (ArCH), 132.6 (HC=N), 133.4 (HC=C) [note that several CHs overlapped]. The product was analyzed by GC/MS; *peak no. 471*, *E*- or *Z*-**19** (54%), $m/z$ (relative intensity); 157 ($M^+$, 22), 117 (100), 102 (6), 91 (27); *peak no. 502*, *E*- or *Z*-**19** (42%), $m/z$ (relative intensity) 157 ($M^+$, 100), 129 (7), 117 (73); HRMS, $C_{11}H_{12}N$ ($MH^+$) requires 158.0970; found; 158.0975.

#### 4.3.19. Methyl 4-(hydroxyimino)-5-methyloct-7-enoate (**23a**)

Sodium acetate (0.89 g, 10.9 mmol) was added to a stirred solution of methyl 5-methyl-4-oxooct-7-enoate (1 g, 5.4 mmol) in ethanol (20 mL) and hydroxylamine hydrochloride (0.65 g, 10.9 mmol). The mixture was stirred for 5 h at reflux temperature. The solution was poured into $H_2O$ (25 mL) and extracted with DCM (3×15 mL). The combined extracts were dried over $MgSO_4$. The solvent was evaporated to dryness to give the crude oxime as a light yellow oil, which was distilled on a Kugelrohr (188 °C, 0.1 mmHg) to give the product as a colorless oil (70%); $^1$H NMR (400 MHz, $CDCl_3$), $\delta_H$ 1.07/1.09 (3H, d, $J$=7.0 Hz, $CH_3$), 2.13 (1H, m, $CH_2$), 2.31 (1H, m, $CH_2$), 2.41–2.69 (5H, m, CH, $CH_2$), 3.68/3.69 (3H, s, $CH_3$), 5.02 (2H, m, $CH_2$), 5.71 (1H, m, CH); $^{13}$C NMR, $\delta_C$ 16.7/17.8 ($CH_3$), 22.8/25.2, 30.2/30.3 ($CH_2$), 31.5/39.5 (CH), 37.8/38.5 ($CH_2$), 52.1/52.1 ($CH_3$), 116.7/117.1 ($CH_2$), 136.3/136.5 (CH), 162.5/163.1, 173.8/174.0 (C); IR, $\nu_{max}$/cm$^{-1}$ 3445, 1740, 1641.

#### 4.3.20. Methyl 5-(hydroxyimino)-6-methylnon-8-enoate (**23b**)

From methyl 6-methyl-5-oxonon-8-enoate (1 g, 5.0 mmol) as described for **23a**. Yellow oil, 73%; $^1$H NMR (400 MHz, $CDCl_3$), $\delta_H$ 1.06/1.10 (3H, d, $J$=6.7 Hz, $CH_3$), 1.79–2.54 (9H, m, CH, $CH_2$), 3.67/3.68 (3H, s, $CH_3$), 5.04 (2H, m, $CH_2$), 5.73 (1H, m, CH), 9.32 (1H, s, OH); $^{13}$C NMR, $\delta_C$ 16.7/17.9 ($CH_3$), 21.5/21.6, 26.6/29.9 ($CH_2$), 31.7/39.0 (CH), 33.8/34.4, 37.8/38.8 ($CH_2$), 52.0 ($CH_3$), 116.7/117.0 ($CH_2$), 136.6/136.7 (CH), 163.1/163.7, 174.2 (C); IR, $\nu_{max}$/cm$^{-1}$ 3325, 1739, 1641.

*4.3.21. 2-(Diphenylmethylleneaminooxy)-2-oxoacetyl chloride*

A solution of benzophenone oxime (1 g, 5.0 mmol) in $Et_2O$ (15 mL) was added dropwise to a stirred solution of oxalyl chloride (0.64 g, 5.0 mmol) in dry $Et_2O$ (10 mL) at −40 °C. After stirring for 1 h at −20 °C the solvent was evaporated to leave a colorless, temperature sensitive, powder (96%). $^1$H NMR (400 MHz, $CDCl_3$), $\delta_H$ 7.23–7.60 (10H, m, CH); $^{13}$C NMR, $\delta_C$ 128.8 (CH)×2, 129.1 (CH)×2, 129.4 (CH)×2, 129.8 (CH)×2, 131.0 (CH), 131.4 (C), 132.3 (CH), 133.8 (C), 155.1 (C), 168.6 (C)×2; IR, $\nu_{max}$/cm$^{-1}$ 2928, 1766, 1763, 1445.

*4.3.22. 2-(Benzylideneaminooxy)-2-oxoacetyl chloride*

White powder; 98%. $^1$H NMR (400 MHz, $CDCl_3$), $\delta_H$ 777.37–7.51 (3H, m, CH), 7.67 (2H, m, CH), 8.45 (1H, s, CH); $^{13}$C NMR, $\delta_C$ 129.4 (C), 129.6 (CH)×2, 132.6 (CH)×2, 133.2 (CH), 159.6 (CH), 172.1, 173.0 (C); IR, $\nu_{max}$/cm$^{-1}$ 2921, 1792, 1767, 1463.

*4.3.23. 2-(2,4-Dimethoxybenzylideneaminooxy)-2-oxoacetyl chloride*

White powder, 93%. $^1$H NMR (400 MHz, $CDCl_3$), $\delta_H$ 3.86 (6H, s, $CH_3$), 6.45 (1H, d, $J$=2.3 Hz, CH), 6.54 (1H, dd, $J$=8.7, 2.3 Hz, CH), 7.86 (1H, d, $J$=8.7 Hz, CH), 8.83 (1H, s, CH); $^{13}$C NMR, $\delta_C$ 56.0 ($CH_3$)×2, 98.5 (CH), 106.6 (CH), 109.8 (C), 129.3 (CH), 155.4 (CH), 161.0, 165.4, 172.1, 172.3 (C); IR, $\nu_{max}$/cm$^{-1}$ 2926, 1791, 1760, 1465.

*4.3.24. Methyl 4,5-dioxo-8-(pent-4-en-2-yl)-1-phenyl-3,6-dioxa-2,7-diazaundeca-1,7-dien-11-oate (**24a**)*

Red oil; mixture of isomers; $^1$H NMR (400 MHz, $CDCl_3$), $\delta_H$ 1.07 (3H, m, $CH_3$), 2.06–2.81 (6H, m, $CH_2$), 3.42 (1H, m, CH), 3.76 (3H, m, $CH_3$), 5.06 (2H, m, $CH_2$), 5.73 (1H, m, CH), 7.32–7.81 (5H, m, CH), 8.51 (1H, c, CH); $^{13}$C NMR, $\delta_C$ 17.0/17.1 ($CH_3$), 24.5/24.4, 29.7/29.8 ($CH_2$), 34.2/39.9 (CH), 38.6/38.7 ($CH_2$), 53.0 ($CH_3$), 110.7 (C), 117.8 ($CH_2$), 129.9 (CH)×2, 133.6 (CH)×2, 134.5, 135.4, 159.2 (CH), 164.9, 165.0, 172.7, 173.3 (C); IR, $\nu_{max}$/cm$^{-1}$ 2976, 1779, 1740, 1642.

*4.3.25. Methyl 1-(2,4-dimethoxyphenyl)-4,5-dioxo-8-(pent-4-en-2-yl)-3,6-dioxa-2,7-diazaundeca-1,7-dien-11-oate (**24b**)*

Red oil; mixture of isomers; $^1$H NMR (400 MHz, $CDCl_3$), $\delta_H$ 1.15 (3H, m, $CH_3$), 2.05–2.80 (6H, m, $CH_2$), 3.46 (1H, m, CH), 3.69 (3H, m, $CH_3$), 3.85 (6H, s, $CH_3$), 5.03 (2H, m, $CH_2$), 5.71 (1H, m, CH), 6.42–6.55 (2H, m, CH), 7.82–7.84 (1H, m, CH), 8.77/8.79 (1H, s, CH); $^{13}$C NMR, $\delta_C$ 16.9/17.7 ($CH_3$), 24.2/25.9, 29.3/30.7 ($CH_2$), 34.5/39.9 (CH), 37.9/38.0 ($CH_2$), 52.2/52.4, 55.9, 56.1 ($CH_3$), 98.5, 106.4 (CH), 110.6 (C), 117.9 ($CH_2$), 129.3, 135.2/135.4, 153.8/154.3 (CH), 160.7, 160.8, 164.9, 165.0, 172.7, 173.3 (C); IR, $\nu_{max}$/cm$^{-1}$ 2975, 1788, 1752, 1731, 1601.

*4.3.26. Methyl 4,5-dioxo-8-(pent-4-en-2-yl)-1,1-diphenyl-3,6-dioxa-2,7-diazaundeca-1,7-dien-11-oate (**24c**)*

Red oil; mixture of isomers; $^1$H NMR (400 MHz, $CDCl_3$), $\delta_H$ 1.03 (3H, m, $CH_3$), 1.93–2.71 (6H, m, $CH_2$), 3.28–3.31 (1H, m, CH), 3.50–3.64 (3H, m, $CH_3$), 4.94 (2H, m, $CH_2$), 5.60 (1H, m, CH), 7.06–7.64 (10H, m, CH); $^{13}$C NMR, $\delta_C$ 17.0/17.7 ($CH_3$), 24.2/25.7, 29.3/30.5 ($CH_2$), 34.3/39.8 (CH), 37.9/38.1 ($CH_2$), 52.2/52.5 ($CH_3$), 118.0 ($CH_2$), 128.7 (CH)×2, 128.9 (CH)×2, 129.4 (CH), 129.5 (CH)×2, 130.7 (CH), 131.6 (C), 131.9 (CH)×2, 134.2 (C), 135.1 (CH), 158.5, 160.2, 166.4, 172.6, 173.2 (C); IR, $\nu_{max}$/cm$^{-1}$ 2977, 1756, 1743, 1641.

*4.3.27. Methyl 4,5-dioxo-8-(pent-4-en-2-yl)-1,1-diphenyl-3,6-dioxa-2,7-diazadodeca-1,7-dien-12-oate (**24d**)*

Red oil; mixture of isomers; $^1$H NMR (400 MHz, $CDCl_3$), $\delta_H$ 1.04/1.13 (3H, d, $J$=6.9 Hz, $CH_3$), 2.05–3.26 (9H, m, CH, $CH_2$), 3.61/3.68 (3H, s, $CH_3$), 4.98 (2H, m, $CH_2$), 5.63 (1H, m, CH), 7.33–7.61 (10H, m, CH); $^{13}$C NMR, $\delta_C$ 16.9/17.7 ($CH_3$), 20.7/21.2, 24.3/25.7, 29.3/30.4, 31.3/33.3 ($CH_2$), 34.2/39.8 (CH), 52.2/52.3 ($CH_3$), 117.7/117.8 ($CH_2$), 128.8 (CH)×2, 128.9 (CH)×2, 129.4 (CH)×2, 129.5 (CH)×2, 130.6/130.7, 131.9, 135.1/135.4 (CH), 131.7, 134.2, 135.0, 158.5, 160.1, 166.4, 173.2 (C); IR, $\nu_{max}$/cm$^{-1}$ 2977, 1755, 1743, 1641.

*4.3.28. Methyl 3-(2,4-dimethyl-3,4-dihydro-2H-pyrrol-5-yl)propanoate (**25a**)*

From benzophenone dioxime oxalate **24c**; yellow oil; 61%; $^1$H NMR (400 MHz, $CDCl_3$), $\delta_H$ 1.03/1.09 (3H, d, $J$=7.2 Hz, $CH_3$), 1.10/1.19 (3H, d, $J$=7.2 Hz, $CH_3$), 1.61 (1H, t, $J$=6.7 Hz, $CH_2$), 2.22–2.84 (6H, m, CH, $CH_2$), 3.60 (3H, s, $CH_3$), 3.77/4.01 (1H, m, CH); $^{13}$C NMR, $\delta_C$ 16.4/17.1, 20.7/21.9 ($CH_3$), 24.9/25.1, 28.7/29.4, 38.5/39.2 ($CH_2$), 43.4/44.5 (CH), 50.6 ($CH_3$), 64.3/64.7 (CH), 172.8, 177.2 (C); IR, $\nu_{max}$/cm$^{-1}$ 1764, 1646.

*4.3.29. Methyl 4-(2,4-dimethyl-3,4-dihydro-2H-pyrrol-5-yl)butanoate (**25d**)*

From benzophenone dioxime oxalate **24d**; yellow oil; 58%; $^1$H NMR (400 MHz, $CDCl_3$), $\delta_H$ 1.01/1.08 (3H, d, $J$=7.1 Hz, $CH_3$), 1.11/1.21 (3H, d, $J$=7.1 Hz, $CH_3$), 1.59 (1H, m, $CH_2$), 1.86 (2H, m, $CH_2$), 2.18–2.35 (5H, m, $CH_2$), 2.71 (1H, m, CH), 3.60 (3H, s, $CH_3$), 3.75/4.01 (1H, m, CH); $^{13}$C NMR, $\delta_C$ 16.4/17.1 ($CH_3$), 20.48 ($CH_2$), 20.9/21.8 ($CH_3$), 29.3/29.4, 32.5/32.6, 38.4/39.1 ($CH_2$), 42.9/44.0 (CH), 50.5 ($CH_3$), 64.1/64.5 (CH), 172.8, 178.2/178.3 (C); IR, $\nu_{max}$/cm$^{-1}$ 1764, 1645.

*4.3.30. Biphenyl-2-carbaldehyde oxime (**29a**)*

Yellow solid; 74%; 108–110 °C; $^1$H NMR (400 MHz, $CDCl_3$), $\delta_H$ 7.21–7.42 (8H, m, CH), 7.84 (1H, d, $J$=7.6 Hz, CH), 8.04 (1H, s, CH); $^{13}$C NMR, $\delta_C$ 126.1, 127.6, 127.7 (CH), 128.4 (CH)×2, 129.7 (CH)×2, 129.8, 130.3 (CH), 136.0, 139.5, 145.2 (C), 149.8 (CH); IR, $\nu_{max}$/cm$^{-1}$ 3179, 1631, 1596, 1481.

*4.3.31. 1-(Biphenyl-2-yl)ethanone oxime (**29b**)*

66%; yellow solid; mp 35–37 °C. Two isomers 9:1. $^1$H NMR (400 MHz, $CDCl_3$), $\delta_H$ 1.58/1.63 (3H, s, $CH_3$), 7.16–7.40 (9H, m, CH); $^{13}$C NMR, $\delta_C$ 16.2 ($CH_3$), 127.4, 127.5 (CH), 128.6 (CH)×2, 129.0 (CH)×2, 129.1, 129.3, 130.4 (CH), 136.8, 140.7, 141.1, 159.2 (C); IR, $\nu_{max}$/cm$^{-1}$ 3228, 1595, 1479.

*4.3.32. Biphenyl-2-yl(phenyl)methanone oxime (**29c**)*

Yellow solid; 56%; 102–104 °C; $^1$H NMR (400 MHz, $CDCl_3$), $\delta_H$ 6.96–7.50 (14H, m, CH), 9.41 (1H, s, OH); $^{13}$C NMR, $\delta_C$ 127.1, 127.2, 127.3, 127.9/128.0 (CH)×2, 128.2/128.3 (CH)×2, 128.5 (CH)×2, 129.2 (CH), 129.4 (CH)×2, 129.6 (CH), 130.1 (CH), 132.2/132.8, 135.6/136.2, 140.6, 141.3, 158.0/158.8 (C).

*4.3.33. 6-Phenylbenzo[d][1,3]dioxole-5-carbaldehyde oxime (**29d**)*

Yellow solid; 68%; 140–142 °C; $^1$H NMR (400 MHz, $CDCl_3$), $\delta_H$ 6.05 (2H, s, $CH_2$), 6.81 (1H, s, CH), 7.30 (2H, m, CH), 7.43 (3H, m, CH), 7.62 (1H, s, CH), 8.02 (1H, s, CH); $^{13}$C NMR, $\delta_C$ 101.9 ($CH_2$), 105.7, 110.4 (CH), 124.0 (C), 128.1 (CH), 128.8 (CH)×2, 130.2 (CH)×2, 138.1, 139.7, 147.8, 149.5 (C), 149.9 (CH); IR, $\nu_{max}$/cm$^{-1}$ 3238, 1613, 1480.

*4.3.34. Biphenyl-2-carbaldehyde dioxime oxalate (**30a**)*

White solid; 97%; $^1$H NMR (400 MHz, $CDCl_3$), $\delta_H$ 7.17/7.24 (4H, m, CH), 7.31–7.41 (10H, m, CH), 7.49 (2H, td, $J$=7.5, 1.5 Hz, CH), 8.02 (2H, d, $J$=7.8 Hz, CH), 8.40 (2H, s, CH); $^{13}$C NMR, $\delta_C$ 126.8 (C)×2, 127.5 (CH)×2, 127.9 (CH)×2, 128.2 (CH)×2, 128.7 (CH)×4, 129.7 (CH)×4, 130.5 (CH)×2, 132.0 (CH)×2, 138.6 (C)×2, 144.0 (C)×2, 157.5 (CH)×2, 163.7 (C)×2; IR, $\nu_{max}$/cm$^{-1}$ 1768, 1734, 1610, 1591, 1451.

*4.3.35. 1-(Biphenyl-2-yl)ethanone dioxime oxalate (**30b**)*

White solid; 95%; $^1$H NMR (400 MHz, $CDCl_3$), $\delta_H$ 1.74 (6H, s, $CH_3$), 7.12–7.53 (18H, m, CH); $^{13}$C NMR, $\delta_C$ 17.4 ($CH_3$)×2, 126.5 (CH)×2, 126.8 (CH)×2, 127.7 (CH)×4, 127.8 (CH)×4, 128.5 (CH)×2, 129.3 (CH)×2, 129.4 (CH)×2, 133.0 (C)×2, 139.0 (C)×2, 139.8 (C)×2, 168.3 (C)×2; IR, $\nu_{max}$/cm$^{-1}$ 1787, 1764, 1684.

*4.3.36. Biphenyl-2-yl(phenyl)methanone dioxime oxalate (**30c**)*

White solid; 97%; $^1$H NMR (400 MHz, $CDCl_3$), $\delta_H$ 6.81–7.58 (28, m, CH); $^{13}$C NMR, $\delta_C$ 126.1 (CH)×2, 126.6 (CH)×2, 127.2 (CH)×4, 127.3 (CH)×4, 127.5 (CH)×2, 127.6 (CH)×2, 128.1 (CH)×4, 128.2

(CH)×4, 129.0 (CH)×2, 129.7 (C)×2, 130.2 (C)×2, 130.5 (CH)×2, 132.8 (C)×2, 138.8 (C)×2, 140.3 (C)×2, 165.1 (C)×2; IR, $\nu_{max}/cm^{-1}$ 1790, 1764, 1653, 1597, 1446.

*4.3.37. 6-Phenylbenzo[d][1,3]dioxole-5-carbaldehyde dioxime oxalate (**30d**)*

White solid; 95%. $^1H$ NMR (400 MHz, $CDCl_3$), $\delta_H$ 5.96/6.00 (2H, s, $CH_2$), 6.71/6.75 (1H, s, CH), 7.13–7.22 (2H, m, CH), 7.28–7.42 (4H, m, CH), 7.91/8.25 (1H, s, CH); $^{13}C$ NMR, $\delta_C$ 101.6/102.1 ($CH_2$), 105.2/106.1, 110.0/110.2, 121.8 (C), 127.5 (CH), 128.4/128.6 (CH×2), 129.7/129.8 (CH×2), 139.2, 142.4, 149.0, 149.4 (C), 149.6/150.5 (CH); IR, $\nu_{max}/cm^{-1}$ 1768, 1734, 1610, 917.

*4.3.38. Phenanthridine (**33a**)*

Yellow crystals; 67%; mp 105–107 °C; $^1H$ NMR[40] (400 MHz, $CDCl_3$), $\delta_H$ 7.62–4.65 (2H, m, CH), 7.71–7.75 (2H, m, CH), 8.08 (1H, d, $J$=8.1, CH), 8.22 (1H, d, $J$=8.2 Hz, CH), 8.61 (1H, dd, $J$=8.1, 1.2 Hz, CH), 8.65 (1H, d, $J$=8.3, CH), 9.32 (1H, s, CH); $^{13}C$ NMR, $\delta_C$ 121.7, 122.1 (CH), 123.9, 126.9 (C), 127.3, 128.4, 128.6, 130.0, 130.8 (CH), 132.3, 144.3 (C), 153.4 (CH).

*4.3.39. 6-Methylphenanthridine (**33b**)*

Yellow crystals; 73%; mp 81–83 °C; $^1H$ NMR[40] (400 MHz, $CDCl_3$), $\delta_H$ 3.02 (3H, s, $CH_3$), 7.57–7.76 (3H, m, CH), 7.79–7.85 (1H, m, CH), 8.11 (1H, dd, $J$=8.1, 1.1 Hz, CH), 8.19 (1H, d, $J$=8.2 Hz, CH), 8.51 (1H, d, $J$=8.1 Hz, CH), 8.59 (1H, d, $J$=8.1 Hz, CH); $^{13}C$ NMR, $\delta_C$ 23.3 ($CH_3$), 122.0, 122.3 (CH), 123.8, 125.9 (C), 126.3, 126.5, 127.3, 128.6, 129.4, 130.5 (CH), 132.5, 143.7, 158.9 (C).

*4.3.40. 6-Phenylphenanthridine (**33c**)*

Yellow crystals; 59%; mp 104–106 °C; $^1H$ NMR[40] (400 MHz, $CDCl_3$), $\delta_H$ 7.50–7.80 (8H, m, CH), 7.88 (1H, ddd, $J$=8.3, 7.0, 1.3 Hz, CH), 8.11 (1H, dd, $J$=8.3, 1.3 Hz, CH), 8.26 (1H, dd, $J$=8.0, 1.6 Hz, CH), 8.64 (1H, d, $J$=8.0 Hz, CH), 8.72 (1H, d, $J$=8.3 Hz, CH); $^{13}C$ NMR, $\delta_C$ 121.9, 122.2 (CH), 123.7, 125.2 (C), 126.9, 127.1, 128.4, 128.7, 128.8, 128.9 (CH), 129.7 (CH)×2, 130.2 (CH), 130.5 (CH)×2, 133.4, 139.8, 143.8, 161.4 (C).

*4.3.41. [1,3]Dioxolo[4,5-j]phenanthridine (trisphaeridine) (**33d**)*

Yellow solid; 59%; mp 144–146 °C; $^1H$ NMR[41] (400 MHz, $CDCl_3$), $\delta_H$ 6.00 (2H, s, $CH_2$), 7.33 (1H, s, CH), 7.62 (1H, td, $J$=7.5, 1.5, CH), 7.62 (1H, td, $J$=7.5, 1.2 Hz, CH), 7.91 (1H, s, CH), 8.13 (1H, dd, $J$=7.4, 1.2 Hz, CH), 8.37 (1H, dd, $J$=8.4, 1.2 Hz, CH), 9.08 (1H, s, CH); $^{13}C$ NMR, $\delta_C$ 99.9 (CH), 101.9 ($CH_2$), 105.5, 122.0 (CH), 123.0, 124.3 (C), 126.7, 128.0, 130.0 (CH), 130.3, 144.0, 148.2, 151.5 (C), 151.7 (CH); IR, $\nu_{max}/cm^{-1}$ 1620, 1580, 1498, 1464; HRMS ($CI^+$), $C_{14}H_{10}NO_2$ requires 224.0712; found: 224.0712.

Crystallographic data (excluding structure factors) for structure **12a** of this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 696935. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax:+44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.uk or at www.ccdc.cam.ac.uk/conts/retrieving.html).

## Acknowledgements

We thank GSK and EaStChem for financial support and Professor A.M.Z. Slawin for the X-ray crystal structure.

## Supplementary data

Preparative procedures for carbonyl compounds and oximes. Photolyses of dioxime oxalates **7a**, **7c**, and **12c**. Crystal data for dioxime oxalate **12a**. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.08.112.

## References and notes

1. Fallis, A. G.; Brinza, I. M. *Tetrahedron* **1997**, *53*, 17543–17594.
2. Bowman, W. R.; Bridge, C. F.; Brookes, P. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1–14.
3. Neta, P.; Fessenden, R. W. *J. Phys. Chem.* **1970**, *74*, 3362–3365.
4. Hudson, R. F.; Lawson, A. J.; Lucken, E. A. C. *J. Chem. Soc., Chem. Commun.* **1971**, 808–809; Hudson, R. F.; Lawson, A. J.; Record, K. A. F. *J. Chem. Soc., Chem. Commun.* **1974**, 488–489.
5. Griller, D.; Mendenhall, G. D.; Van Hoof, W.; Ingold, K. U. *J. Am. Chem. Soc.* **1974**, *96*, 6068–6070.
6. Blake, J. A.; Pratt, D. A.; Lin, S.; Walton, J. C.; Mulder, P.; Ingold, K. U. *J. Org. Chem.* **2004**, *69*, 3112–3120.
7. Forrester, A. R.; Gill, M.; Meyer, C. J.; Sadd, J. S.; Thomson, R. H. *J. Chem. Soc., Perkin Trans. 1* **1979**, 606–611.
8. Forrester, A. R.; Gill, M.; Sadd, J. S.; Thomson, R. H. *J. Chem. Soc., Perkin Trans. 1* **1979**, 612–615.
9. Forrester, A. R.; Gill, M.; Thomson, R. H. *J. Chem. Soc., Perkin Trans. 1* **1979**, 616–620.
10. Forrester, A. R.; Napier, R. J.; Thomson, R. H. *J. Chem. Soc., Perkin Trans. 1* **1981**, 984–987.
11. Zard, S. Z. *Synlett* **1996**, 1148–1154.
12. Kaim, L. E.; Meyer, C. *J. Org. Chem.* **1996**, *61*, 1556–1557.
13. Takai, K.; Katsura, N.; Kunisada, Y. *Chem. Commun.* **2001**, 1724–1725.
14. Bowman, W. R.; Bridge, C. F.; Brookes, P.; Cloonan, M. O.; Leach, D. R. *J. Chem. Soc., Perkin Trans. 1* **2002**, 58–68; Bowman, W. R.; Cloonan, M. O.; Fletcher, A. J.; Stein, T. *Org. Biomol. Chem.* **2005**, *3*, 1460–1467.
15. Boivin, J.; Fouquet, E.; Zard, S. Z. *Tetrahedron Lett.* **1991**, *32*, 4299–4302.
16. Boivin, J.; Schiano, A.-M.; Zard, S. Z. *Tetrahedron Lett.* **1992**, *33*, 7849–7852.
17. McCarroll, A. J.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **2000**, 2399–2409.
18. Alonso, R.; Campos, P. J.; Garcia, B.; Rodriguez, M. A. *Org. Lett.* **2006**, *8*, 3521–3523; Alonso, R.; Campos, P. J.; Rodrıguez, M. A.; Sampedro, D. *J. Org. Chem.* **2008**, *73*, 2234–2239.
19. Mikami, T.; Narasaka, K. *Chem. Lett.* **2000**, 338–339.
20. Narasaka, K.; Uchiyama, K.; Ono, A.; Hyashi, Y. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2945–2955; Narasaka, K.; Uchiyama, K.; Hyashi, Y. *Tetrahedron* **1999**, *55*, 8915–8930; Narasaka, K.; Mikami, T. *C. R. Acad. Sci. Paris, Chimie* **2001**, 477–486; Narasaka, K.; Kitamura, M.; Yoshida, M. *Chem. Lett.* **2002**, 144–145.
21. Nanni, D.; Pareschi, P.; Rizzoli, C.; Sgarabotto, P.; Tundo, A. *Tetrahedron* **1995**, *51*, 9045–9062; Cammagi, C. M.; Leardini, R.; Nanni, D.; Zanardi, G. *Tetrahedron* **1998**, *54*, 5587–5598; Leardini, R.; McNab, H.; Minozzi, M.; Nanni, D. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1072–1078; Nanni, D. In *Radicals in Organic Synthesis*; Renaud, P., Sibi, M., Eds.; Wiley: Weinheim, 2001; Vol. 2, pp 44–61.
22. Portela-Cubillo, F.; Scott, J. S.; Walton, J. C. *Chem. Commun.* **2007**, 4041–4043; Portela-Cubillo, F.; Scott, J. S.; Walton, J. C. *J. Org. Chem.* **2008**, *73*, 5558–5565.
23. Le Tadic-Biadatti, M.-H.; Callier-Dublanchet, A.-C.; Horner, J. H.; Quiclet-Sire, B.; Zard, S. Z.; Newcomb, M. *J. Org. Chem.* **1997**, *62*, 559–563.
24. Scanlan, E. M.; Walton, J. C. *Helv. Chim. Acta* **2006**, *89*, 2133–2143; Scanlan, E. M.; Slawin, A. M. Z.; Walton, J. C. *Org. Biomol. Chem.* **2004**, *2*, 716–724; Scanlan, E. M.; Walton, J. C. *Chem. Commun.* **2002**, 2086–2087.
25. Portela-Cubillo, F.; Scanlan, E. M.; Scott, J. S.; Walton, J. C. *Chem. Commun.* **2008**, 4189–4191.
26. Jochims, J. C.; Hehl, S.; Herzberger, S. *Synthesis* **1990**, 1128–1133.
27. For our purpose this was not important because each *Z*/*E* isomer gave the same iminyl radical on fission of the N–O bond.
28. Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.
29. Forrester, A. R.; Neugebauer, F. A. In *Landolt-Bornstein, Magnetic Properties of Free Radicals*; Fischer, H., Hellwege, K.-H., Eds.; Springer: Berlin, 1979; Vol. II9c1, p 115.
30. See for example: Vargas-Sanchez, M.; Couty, F.; Evano, G.; Prim, D.; Marrot, J. *Org. Lett.* **2005**, *7*, 5861–5864.
31. Lertpibulpanya, D.; Marsden, S. P. *Org. Biomol. Chem.* **2006**, *4*, 3498–3504.
32. Rosa, A. M.; Prabhakar, S.; Lobo, A. M. *Tetrahedron Lett.* **1990**, *31*, 1881–1884.
33. Harayama, T.; Akamatsu, H.; Okamura, K.; Miyagoe, T.; Akiyama, T.; Abe, H.; Takeuchi, Y. *J. Chem. Soc., Perkin Trans. 1* **2001**, 523–528.
34. Banwell, M. G.; Lupton, D. W.; Ma, X.; Renner, J.; Sydnes, M. O. *Org. Lett.* **2004**, *6*, 2741–2744.
35. Motorina, I. A.; Fowler, F. W.; Grierson, D. S. *J. Org. Chem.* **1997**, *62*, 2098–2105.
36. Gawley, R. E.; Enrico, E. J. *J. Org. Chem.* **1984**, *49*, 1946–1951.
37. Hwu, J. R.; Tseng, W. N.; Patel, H. V.; Wong, F. F.; Horng, D.-N.; Liaw, B. R.; Lin, L. C. *J. Org. Chem.* **1999**, *64*, 2111–2218.
38. Reisch, J. *Arch. Pharm.* **1972**, *305*, 85–87.
39. Tiecco, M.; Testaferri, L.; Tingoli, M.; Bagnoli, L.; Marini, F. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1989–1993.
40. Lysen, M.; Kristensen, J. L.; Vedsø, P.; Begtrup, M. *Org. Lett.* **2002**, *4*, 257–259.
41. Sanz, R.; Fernandez, Y.; Castroviejo, M. P.; Perez, A.; Fananas, F. J. *Eur. J. Org. Chem.* **2007**, 62–69.