Exploitation of aldoxime esters as radical precursors in preparative and EPR spectroscopic roles

Andrew J. McCarroll and John C. Walton *

University of St. Andrews, School of Chemistry, St Andrews, Fife, UK KY16 9ST.
E-mail: jcw@st-and.ac.uk

Received (in Cambridge, UK) 6th September 2000, Accepted 12th October 2000
First published as an Advance Article on the web 15th November 2000

Photolyses of aldoxime esters, containing a considerable range of alkyl groups, lead to cleavage of their N–O bonds and formation of aryliminyl and alkyl radicals. The process was found to be favoured by 4-methoxyacetophenone as a photosensitiser and by methoxy substituents in the aryl rings. 4-Nitro- and pentafluoro-substitutions of the aryl rings were, on the other hand, deleterious. The intermediate iminyl radicals, together with primary, secondary and tertiary alkyl radicals were characterised by 9 GHz EPR spectroscopy. Cyclopropyl, CF_3, and CCl_3 radicals were probably also formed, but were too reactive for direct EPR spectroscopic detection. Photosensitised reaction of benzophenone oxime *O*-nonanoyl ester produced the diphenylmethaniminoxyl, as well as the expected *n*-octyl and iminyl radicals. This indicated that O–C bond scission accompanied O–N scission for this ketoxime ester.

At higher temperatures the C-centred radicals added to the starting oxime esters to produce alkoxyaminyl radicals that were also spectroscopically detected in some cases. No evidence for abstraction of the iminyl hydrogen by *tert*-butoxyl radicals was obtained. Instead, the *t*-BuO$^{\bullet}$ radicals added to the C=N double bonds of the oxime esters. Similarly, chlorine abstraction from alkylbenzohydroximoyl chlorides by trimethyltin radicals did not take place. Preparative scale experiments with oxime esters containing suitably unsaturated alkyl groups showed that good yields of cyclised products could be obtained in the presence of the photosensitiser. This process constitutes a general method by which carboxylic acids or acid chlorides can be converted into alkyl radicals and hence to cyclised derivatives.

Introduction

A variety of oxime esters containing weak N–O bonds are easily made from aldehyde (or ketone) oximes and carboxylic acids (or acyl halides). They constitute a category of precursors for carbon-centred and iminyl radicals with promise of considerable generality, but so far exploitation has been minimal. Hasebe *et al.* showed that benzophenone oxime esters [Ph_2-C=NOC(O)R] functioned well as photolytic sources of alkyl (R$^{\bullet}$) and diphenyliminyl radicals and used them in preparations of alkyl aromatics,[1,2] alkyl chlorides,[2] and alkanes.[2] Radical induced homolysis of oxime benzoates by tributylstannane was found to be a useful method for generating iminyl radicals,[3,4] which were also produced, without the need for toxic organotin compounds, by use of Ni powder and acetic acid.[5,6] In one surprising reaction, a 6-*endo* cyclisation onto the *nitrogen* of an oxime ether was described.[7]

Compound types suitable for clean photochemical or thermal generation of free radicals are quite limited, and therefore potential new precursors are of special interest. The advantages of oxime esters [R^1R^2C=NOC(O)R] include their ease of handling and characterisation, in comparison with peroxides or azo-compounds, and therefore further investigation of the scope and limitations of their free radical chemistry was an attractive prospect. In particular, EPR spectroscopy had rarely been used to study intermediates formed in photochemical or thermal reactions of oxime esters. Our objective, therefore, was to investigate the homolytic reactions of a range of oxime esters on direct and sensitised photolysis. EPR spectroscopy was employed to characterise intermediates in these reactions, complemented by end product analyses. The study focused mainly on aldoxime esters [Ar(H)C=NOC(O)R] because the oximinyl hydrogen proved beneficial in the spectroscopic work. A selection of aryl and alkyl groups was chosen to compare the effects of substituents with different electron demands and to probe the efficiency of cyclisation of unsaturated alkyl groups. Part of this research was previously reported in a communication.[8]

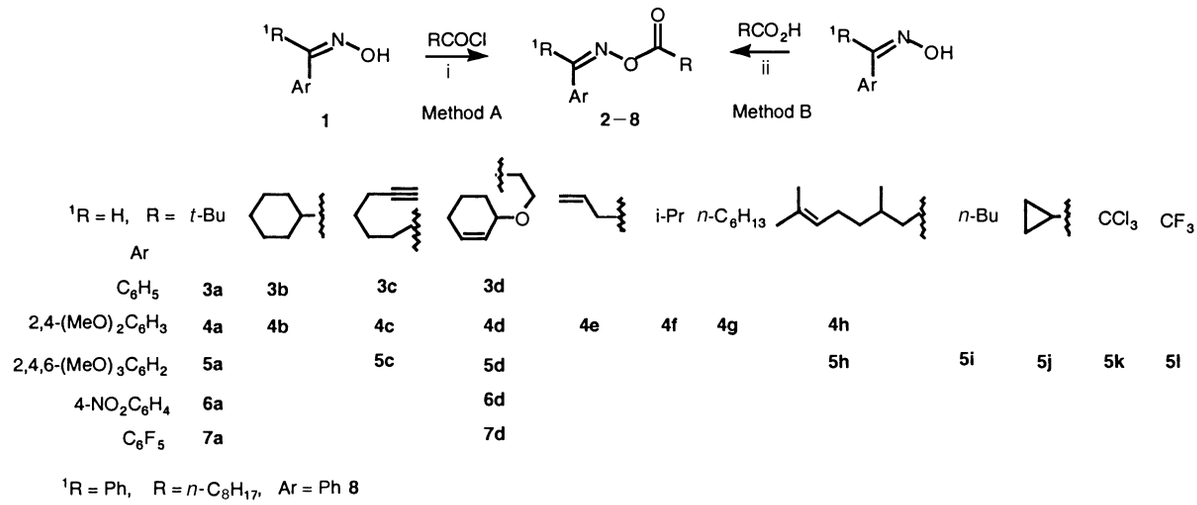
Results and discussion

Preparation of oxime esters

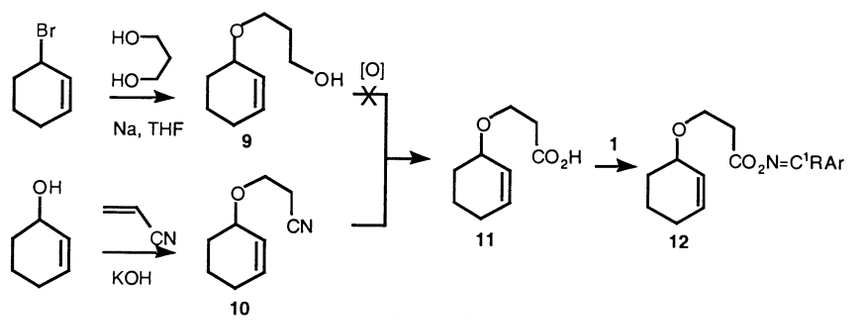
A selection of oxime esters **2** was synthesised, generally in good yield, from one of two methods (Scheme 1). Several preparations simply involved adding an oxime to the chosen acid chloride, mediated by triethylamine in DCM (Method A). The alternative method, which involved DCC coupling of an oxime with the corresponding carboxylic acid (catalysed by DMAP), was usually more convenient and often led directly to crystalline products without the need to resort to column chromatography (Method B). The oximes (**1**) chosen for investigation, which were prepared using standard methods from the corresponding aldehyde and hydroxylamine hydrochloride, were benzaldoxime,[9] 4-nitrobenzaldoxime,[9] pentafluorobenzaldoxime,[10] 2,4-dimethoxybenzaldoxime,[11] 2,4,6-trimethoxybenzaldoxime,[12] and benzophenone oxime.[9] Oxime esters **3**–**7a**, **b**, **e**–**g**, **i**–**l** and **8** were prepared mainly for EPR investigations and to examine intermolecular addition, whilst **3**–**7c**, **d**, and **h** were prepared primarily for examination of intramolecular reactions. *O*-Trichloromethyl oxime derivatives were reported to be unstable.[13] We found this to apply to *O*-trichloromethyl and *O*-trifluoromethyl 2,4,6-trimethoxybenzaldoximes **5k** and **5l**.

The preparation of *O*-(cyclohexenyloxy)propionyl oximes **12** was non-trivial. Several routes to the carboxylic acid **11**, *via* hydroxy ether **9** and nitrile **10**, were explored (Scheme 2). 3-(Cyclohex-2-enyloxy)propan-1-ol **9** was made successfully

DOI: 10.1039/b007212p



Scheme 1 *Reagents and conditions*: (i) NEt_3, DCM; (ii) DCC, DMAP, DCM.



Scheme 2

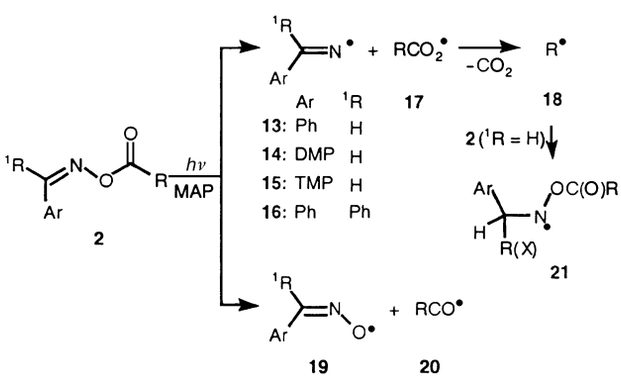
from 3-bromocyclohexene and propane-1,3-diol using sodium, but proved difficult to oxidise. Three oxidation methods were attempted; the standard method, using chromic acid[9] proved to be too harsh, and the molecule fell apart. Oxidation using TEMPO, bleach, and sodium bromide[14,15] gave no product. An attempt to split the oxidation into two separate stages *i.e.* first to the aldehyde by Swern oxidation,[16] then using an Oxone system[17] to oxidise the aldehyde to the acid, failed at the second stage. Eventually a route was found involving Michael addition of acrylonitrile to cyclohexenol, using a catalytic amount of potassium hydroxide.[18,19] The nitrile **10** was hydrolysed to the acid **11** using sodium peroxide in warm water.[20,21]

The oximes, and oxime esters, are believed to be the *syn* isomers. The synthesis of benzaldoxime **3** was specific to the *syn* isomer,[9] but the other reported syntheses did not indicate which isomers were formed. Pejković-Tadić *et al.* reported that the oximinyl hydrogen chemical shifts of various substituted benzaldoximes were dramatically different for the *syn* and *anti* isomers.[22] All the *syn* isomers had protons with $\delta > 8$, while the *anti* isomers had $\delta < 7.5$. This distinction enabled us to assign the configuration of **3**–**7** and **8** as *syn* with confidence.

Aldoxime esters **3** (Ar = Ph) displayed strong UV absorption bands at 208 and 254 nm ($\varepsilon = 10–22 \times 10^3$ and $9–18 \times 10^3$ $mol^{-1}\,dm^3\,cm^{-1}$ respectively). Inclusion of methoxy substituents in the aryl group (**4**, **5**) induced additional strong absorption bands at longer wavelengths ($\lambda_m = 273$, 312 nm) and this implied that photo-dissociation to radicals might be more efficient.

EPR spectroscopic investigation of radical generation from oxime esters

Photolysis (500 W Hg arc, unfiltered) of a deoxygenated *tert*-butylbenzene solution of hexynyl aldoxime ester **3c** in the resonant cavity of a 9 GHz EPR spectrometer gave rise to



MAP = *p*-methoxyacetophenone, DMP = 2,4-dimethoxyphenyl, TMP = 2,4,6-trimethoxyphenyl

Scheme 3

a weak spectrum of iminyl radical PhCH=N$^\bullet$ (**13**) with EPR parameters identical to those reported in the literature,[23] including a characteristically large hyperfine splitting (hfs) from the iminyl hydrogen (Table 1). A persistent radical [a(N) = 7.14 G, a(H) = 1.45 G, g = 2.0097], possibly an acylaminoxyl, was observed on prolonged photolysis. Slightly better quality EPR spectra were obtained from photolysis of the *tert*-butyl oxime ester **3a** which showed weak spectra of both the iminyl radical and the *tert*-butyl radical. Addition of small amounts of 4-methoxyacetophenone (MAP) as photosensitiser[24] to samples prior to degassing, dramatically improved the spectral intensity. To obtain an indication of the optimum quantities of sensitiser required, samples of **3a** with various concentrations of sensitiser were prepared and the relative iminyl and *tert*-butyl radical concentrations were determined by double integration of suitable EPR peaks. It was found that, while maximum

Table 1 9.5 GHz EPR spectroscopic observations on sensitised photolyses of oxime esters in *tert*-butylbenzene solution[a]

Oxime ether	*T*/K	Iminyl ($Im^{\bullet}$)	Alkyl[b] ($R^{\bullet}$)	Aminyl ($Am^{\bullet}$)	$[Im^{\bullet}]/[R^{\bullet}]$	$[Im^{\bullet}]/[Am^{\bullet}]$ (*T*/K)
3a	250	**13**[c]	*t*-Bu		1.0	0.50 (270)
3c	220	**13**	n.o.	n.o.		
4a	250	**14**[d]	*t*-Bu		—	0.48 (280)
4b	240	**14**	n.o.			0.52 (280)
	300	**14**	n.o.			0.30 (300)
4c	250	**14**	Hex-5-ynyl	n.o.		
4d	300	**14**	n.o.			0.25 (300)
4e	235	**14**	Allyl	n.o.	2.7	
	270	**14**	n.o.	n.o.	1.2	
4f	240	**14**	i-Pr	n.o.	2.9	
4g	205	**14**	Hexan-1-yl	n.o.	0.52	
	275	**14**	Hexan-1-yl	n.o.	2.2	
4h	250	**14**	DMH[e]	n.o.	2.5	
5a	240	**15**	*t*-Bu	n.o.	1.1	
5h	285	**15**[f]	DMH[e]	n.o.	6.2	
5i	220	**15**	*n*-Bu	n.o.	2.3	
	300	**15**	*n*-Bu	n.o.	1.7	
5j	220	**15**	n.o.[g]	n.o.		
5k	220	**15**	n.o.	n.o.		
5l	220	**15**	n.o.[h]	n.o.		
8	240	**16**[j]	Octan-1-yl	n.o.[i]	4.3	

[a] Sensitised with 4-methoxyacetophenone. All spectra were satisfactorily computer simulated using Bruker Simfonia software. Hfs in G (10 G = 1 mT). [b] All radicals $R^{\bullet}$ had spectral parameters identical to those given in the literature; n.o. = not observed. [c] a(N) = 9.9, a(H) = 79.9, a(2H) = 0.46, a(2H) = 0.42 G, g = 2.0034 at 225 K. [d] a(N) = 10.0, a(H) = 81.2, a(2H) = 0.42 G, g = 2.0034 at 250 K. [e] DMH = 2,6-dimethylhept-5-en-1-yl; a(2H) = 22.5, a(1H) = 30.6 G, g = 2.0027 at 280 K. [f] a(N) = 10.7, a(H) = 84.0 G, g = 2.0034 at 300 K. [g] 1-Cyclopropyl-3-*tert*-butylcyclohexadienyl radical **22** observed in Ph-*t*-Bu solvent. [h] Unidentified radical, possibly **23**, observed; see text. [i] Iminoxyl **19** (^{1}R = Ph = Ar) was observed: a(N) = 31.6, a(2H) = 1.3 G, g = 2.0066, $[Im^{\bullet}]/[ImO^{\bullet}]$ = 1.4 at 240 K. [j] a(N) = 10.1 G, g = 2.0034 at 240 K.

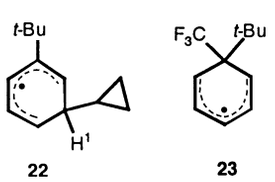
signal intensities were obtained with 0.5–1 mol equiv. of MAP, excellent results could still be obtained with as little as 0.1 mol equiv. Spectra were enhanced by a maximum factor of *ca*. 5.

2,4-Dimethoxybenzaldoxime esters **4** gave noticeably stronger signals than the unsensitised benzaldoxime derivatives. Again, addition of MAP resulted in still stronger spectra. For example, illumination of *O*-isopropyl 2,4-dimethoxybenzaldoxime **4f** showed the desired isopropyl radical plus the iminyl radical **14**. Primary alkyl radicals could also be observed using this method. The hex-5-ynyl radical was detected during photolyses of *O*-hept-6-ynoyl 2,4-dimethoxybenzaldoxime **4c** (Table 1). The hexan-1-yl radical could be observed clearly enough from *O*-heptanoyl 2,4-dimethoxybenzaldoxime **4g** for resolution of γ-hydrogen splittings. *O*-Vinylacetyl 2,4-dimethoxybenzaldoxime **4e** gave excellent spectra of the desired allyl radical (Table 1).

2,4,6-Trimethoxybenzaldoxime esters also gave stronger spectra than derivatives of benzaldoxime, but several of the precursors (**5**) were virtually insoluble at the temperatures required for EPR spectroscopy. The effect of the sensitiser was less dramatic in spectra from these precursors. The primary radical, which would be expected to form from *O*-(cyclohex-2-enyloxy)propionyl 2,4,6-trimethoxybenzaldoxime **5d** (prior to cyclisation) was not observed, although strong signals from iminyl radical **15** were present. Very weak spectra of the desired primary radical were obtained from *O*-2,6-dimethylhept-5-enylcarbonyl 2,4,6-trimethoxybenzaldoxime **5h** (Table 1). This identification was supported by the measured *g*-factor of 2.0027. Also present was a species having a(2H) = 1.1 G, g = 2.00056 at 240 K; identified as the arylacyl radical 2,4,6-$(MeO)_3C_6H_2C(O)^{\bullet}$ with characteristically small H-hfs and small *g*-factor.[25] It is likely that this was formed by H-abstraction from traces of aldehyde either accompanying the oxime ether precursor, or from *in situ* hydrolysis.

The results indicated that oxime esters **3**–**5** underwent homolysis of their weak N–O bonds on direct and photosensitised UV photolysis to afford mixtures of iminyls **13**–**16** and acyloxyl radicals **17**. The latter rapidly lost CO_2 to release the corresponding alkyl radicals **18** (Scheme 3). Strong spectra of secondary, tertiary and delocalised C-centred radicals were usually obtained but weaker signals were generally observed for primary radicals and this may have been due to slower decarboxylation steps. On the whole, oxime esters ArCH=NOC(O)R contrasted with oxime ethers ArCH=NOR which did not undergo direct or sensitised photolyses of their N–O bonds efficiently enough to produce EPR spectra.[26] EPR spectra from benzaldoxime esters containing 4-nitro- (**6**) and pentafluoro-substituents (**7**) were also examined, but neither iminyl radicals nor C-centred radicals were detected, although some adduct species did appear (see below).

Attempts were made to observe σ-radicals using appropriate oxime esters as precursors. Photolysis of *O*-cyclopropylcarbonyl 2,4,6-trimethoxybenzaldoxime **5j**, under EPR conditions in *tert*-butylbenzene, led to the observation of the expected iminyl radical accompanied by a radical, displaying five separate hfs, that was well simulated with the following parameters: a(H) = 35.11 G, a(H) = 13.23 G, a(H) = 9.24 G, a(H) = 8.07 G, a(H) = 2.75 G. The σ-type cyclopropyl radical added to the *tert*-butylbenzene solvent at the *meta* position resulting in the 1-cyclopropyl-3-*tert*-butylcyclohexadienyl radical **22**. *meta*-Additions of σ-type radicals to *tert*-butylbenzene have been reported previously,[27] and H^1 hfs of ~36 G are characteristic. The oxime ester photolysis was repeated in cyclopropane, but only iminyl spectra could be observed over a wide temperature range, possibly because *O*-cyclopropylcarbonyl 2,4,6-trimethoxybenzaldoxime **5j** was not very soluble in cyclopropane.



22 **23**

As previously mentioned, *O*-trichloromethylcarbonyl 2,4,6-trimethoxybenzaldoxime **5k** and *O*-trifluoromethylcarbonyl 2,4,6-trimethoxybenzaldoxime **5l** were found to be unstable. Both samples were used immediately after preparation without

Table 2 EPR parameters of aminyl radicals [ArCH(X)N$^{\bullet}$OC(O)R] (**21**) obtained from aldoxime esters in *tert*-butylbenzene solution

Oxime ether	Ar	R	X	Conditions	Temp/K	*g*-Factor	*a*(N)/G	*a*(H)/G
3a	Ph	*t*-Bu	*t*-Bu	DTBP, *hv*	270	2.0045	14.5	20.3
3d	Ph	HOE[a]	[c]	DTBP, *hv*	320		15.0	19.0
3d	Ph	HOE[a]	[c]	MAP, *hv*	280		14.9	18.7
3c	Ph	C_6H_9[b]	*t*-BuO$^{\bullet}$	BPOO, Heat	340		14.4	22.2
4a	DMP	*t*-Bu	*t*-BuO$^{\bullet}$	BPOO, Heat	345		14.5	23.8
3b	DMP	*c*-C_6H_{12}	*c*-C_6H_{12}	MAP, *hv*	280	2.0045	15.0	18.5
4d	DMP	HOE[a]	[c]	MAP, *hv*	300	2.0046	14.8	18.6
7a	C_6F_5	*t*-Bu	*t*-Bu	DTBP, *hv*	370		14.5	26.9[d]

[a] HOE = 2-(cyclohex-2-enyloxy)ethyl. [b] Hex-5-ynyl. [c] Probably the cyclised radical; 1-oxabicyclo[4.3.0]nonan-5-yl radical (see text). [d] Additional hfs *a*(2F) = 2.1 G.

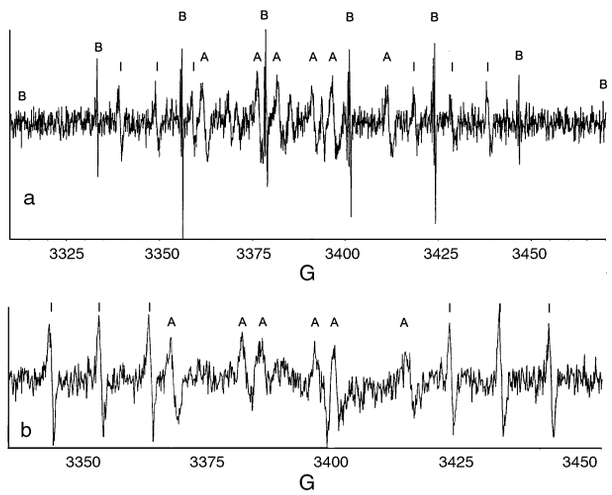


Fig. 1 (a) Upper frame: 9.5 GHz EPR spectrum obtained from oxime ester **3a** at 270 K. *t*-Bu$^{\bullet}$ radical indicated by "B", iminyl radical **13** indicated by "I" and aminyl radical **21** (R = *t*-Bu) indicated by "A". (b) Lower frame: 9.4 GHz EPR spectrum obtained from oxime ester **4b** at 280 K. Iminyl radical **14** indicated by "I" and aminyl radical **21** (R = cyclohexyl) indicated by "A".

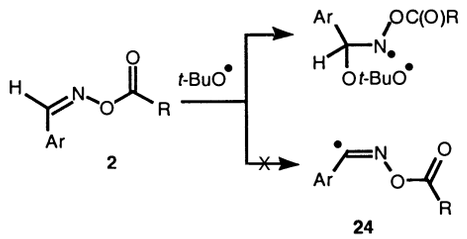
additional purification. Photolysis of **5k** gave only the spectrum of iminyl radical **15**, but **5l** showed this iminyl radical together with a radical type previously unseen in this investigation [*a*(2H) = 1.95 G, *a*(2H) = 6.87 G, *a*(1H) = 9.95 G]. One possibility is *ipso* addition to form radical **23**. This seems unlikely for steric reasons, although the hfs fit this radical quite well. Neither the trichloromethyl nor the trifluoromethyl radical was observed in these photolyses.

The ratio of the concentrations of the alkyl and iminyl radicals depended on temperature and on the nature of R. For example, from **4e** (R = allyl) very intense spectra mainly of allyl were obtained, particularly for low power and low modulation amplitude whereas for **5i** (R = *n*-Bu) the spectra were dominated by the iminyl signals and in general primary alkyls were difficult to detect. Scission of the N–O bond in **2** should initially produce equal amounts of an iminyl and an acyloxyl radical **17** (Scheme 2). However, the experimental ratio of iminyl to alkyl radicals [Im$^{\bullet}$]/[R$^{\bullet}$] (Table 1) will depend on the completeness of decarboxylation of **17** as well as radical termination efficiencies. For most of the oxime esters the observed ratio was within a factor of two or three of expectation, except for some primary radicals. The observed differences from unity in the [Im$^{\bullet}$]/[R$^{\bullet}$] ratios can be attributed to minor differences in the rates of their termination reactions, except for the primary alkyls, for which slower decarboxylation steps may have depressed the alkyl concentrations.

The EPR spectra obtained from several of the oxime esters contained 6 line signals due to an additional radical. For example, the spectra acquired during MAP sensitised photolyses of **3a** and **4b** contained signals due to iminyl, alkyl (**18**) and an additional radical, which showed up most clearly at higher temperatures ($T > 260$ K, see Fig. 1). The hfs, and the measured *g*-factors of *ca*. 2.0048 (Table 2) were similar to the EPR parameters of alkoxyaminyl radicals such as i-PrN$^{\bullet}$OCH$_3$ [$g = 2.0046$, $a(\mathrm{N}) = 13.96$, $a(1\mathrm{H}) = 18.8$, $a(3\mathrm{H}) = 2.56$ G at 210 K in toluene],[28,29] and to the parameters reported for adduct alkoxyaminyl radicals obtained from addition of several radical types to a range of oxime ethers.[26] We therefore attribute the spectra to adduct aminyl radicals **21** (Scheme 3). Although it is possible that the iminyl radicals might add to the oxime esters, it is most likely, in view of the significant differences in the hfs measured for esters having different alkyl substituents (Table 2) that the observed aminyls were formed by alkyl radical addition. The measured ratios of the iminyl to aminyl radicals [Im$^{\bullet}$]/[Am$^{\bullet}$] (Table 1) indicate that adduct aminyls were most readily formed at higher temperatures and for tertiary and secondary alkyl radicals. Aminyls were not detected when the co-radical was a primary alkyl, the only apparent exception being the 2-(cyclohex-2-enyloxy)ethyl radical from oxime ester **4d**. It is noteworthy, however, that this particular primary radical was not detected (from **4d** or any of **3d**–**7d**) and it is possible that the trapped radical was actually the secondary cyclised radical, *i.e.* the 2-oxabicyclo[4.3.0]nonan-6-yl radical. The inefficient addition of primary radicals could be because of their generally lower concentrations (see above) or possibly because addition was faster for more nucleophilic species.

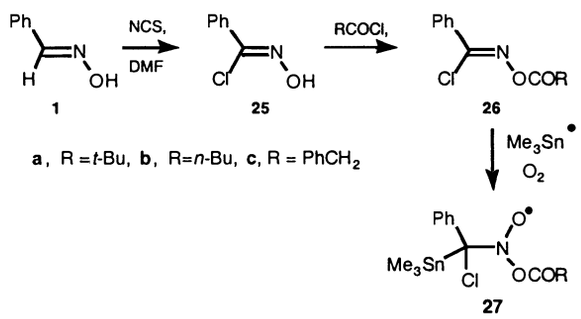
To test for direct addition of *t*-BuO$^{\bullet}$ radicals to oxime esters, di-*tert*-butyl peroxyoxalate (BPOO) was thermally decomposed in the presence of **3c** and **4a** in *tert*-butylbenzene solution. Weak EPR spectra of the aminyl adducts ArCH(O*t*-Bu)-N$^{\bullet}$OC(O)R were detected in both cases (Table 2) although a second, unidentified, radical was also present in spectra from **4a**. Spectra were also obtained by photolysis of solutions of several oxime esters in di-*tert*-butyl peroxide (DTBP). Abstraction of the iminyl hydrogen appeared to be a possibility under these conditions. However, the EPR spectra were often similar to those obtained during the MAP photosensitised reactions. For example, illumination of a solution of **3a** in DTBP gave rise to a spectrum similar to that shown in Fig. 1a and containing signals from *t*-Bu$^{\bullet}$, iminyl **13** and an aminyl with hfs appropriate for the *t*-Bu$^{\bullet}$ adduct (Table 2). Several of the other oxime esters also gave iminyl and aminyl radicals, but spectra under these conditions tended to be complicated by additional signals from aminoxyl species presumably formed in oxidations mediated by the presence of excess DTBP. No spectra corresponding to imidoyl radicals **24** (Scheme 4) were observed at any temperature, or with any of the oxime esters, and no evidence for abstraction of the iminyl hydrogen was obtained. The reactions in DTBP were probably dominated by photodissociation of the N–O bonds of the oxime esters, and reactions of *t*-BuO$^{\bullet}$ radicals were minor.

Because imidoyl radicals **24** were at no time observed by EPR spectroscopy of oxime esters, an alternative method of



Scheme 4

generation of these radicals by halogen abstraction from *O*-acylbenzohydroximoyl chlorides **26** was investigated. Benzohydroximoyl chloride **25** was prepared by the action of NCS in DMF on the parent oxime,[30] and acylated in DCM with triethylamine and an acid chloride in moderate yields (Scheme 5).



Scheme 5

Degassed solutions of **26a**, **b** or **c** and hexamethylditin in *tert*-butylbenzene were illuminated by a 500 W super pressure mercury lamp under EPR conditions. All three precursors led to the formation of mixtures of several radicals. The major radical in each case was persistent and had a large nitrogen hfs [a(N) ~ 26 G] (Table 3). While oximidoyl radicals of type **24** are practically unknown in the literature, imidoyl radicals, RC$^{\bullet}$=NR′, have been formed and investigated by EPR spectroscopy. They were generated by H-abstraction from imines,[31,32] and by radical addition to isonitriles.[33] Derivatives with R = Ph did not give resolvable spectra (the line widths were very large), but reported values for a(N) were in the range of 1.4–2.4 G for similar radicals with R = alkyl. For R′ = *t*-Bu, Davies *et al.*[32] and Blum and Roberts[33] observed the spectrum of *t*-Bu$^{\bullet}$ above 220 K, due to the radical dissociating. Comparison with literature data indicated that the observed radical was not an imidoyl radical, nor was it an iminoxyl radical such as PhC(Cl)=NO$^{\bullet}$. Related iminoxyl radicals all had nitrogen hfs of 30–31 G in *tert*-butylbenzene (for both *syn* and *anti* isomers).[34] Acyloxyaminoxyls are also extremely persistent, and the observed radicals may have been **27**, formed by addition of the stannyl radical followed by oxidation with a trace amount of oxygen. Related α-chloroalkoxyaminoxyl radicals have previously been observed in water,[35] benzene[36] and trichlorofluoromethane.[36] Kayen *et al.* reported a(Cl) = 3.5–3.8 G, a(N) = 22.7–24.2 G in benzene or trichlorofluoromethane.[36] However, Norman and co-workers commented that β-chlorine hfs are usually small or undetectable, and that nitrogen splittings are usually in the range 24–29 G.[35] Thus, the hfs we observed fit structure **27** reasonably well. The other radicals observed from the benzohydroximoyl chlorides **26** had a(N) values of either *ca.* 15 or *ca.* 7 G and were probably alkyl and acylaminoxyls formed in further oxidation processes. Oximidoyl radicals **24** could not therefore be observed by hydrogen or chlorine abstraction from oxime esters.

Illumination of the *tert*-butyl ester 4-nitrobenzaldoxime **6a** (in DTBP, *t*-BuPh or DMF) led to a persistent radical

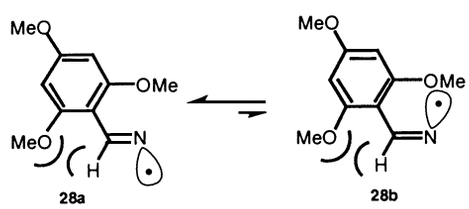
Table 3 EPR data of radicals generated from *O*-acylbenzohydroximoyl chlorides **26**

Precursor	T/K [a]	a(N)/G	a(Other)/G	Identity
26a	320	26.3	0.73 (1Cl) 0.73 (4H) 0.35 (1H)	**27a**
26b	280	26.8 [b]		**27b**
26c	320	26.9 [b]		**27c**

[a] *tert*-Butylbenzene solvent. [b] Unresolved.

[a(N) = 12.6, a(2H) = 3.0, a(2H) = 1.1, a(N) = 1.1, a(1H) = 0.6 G at 270 K]. One possible explanation was that the radical anion of the oxime or ester, formed in some electron transfer process, was being observed. However, the published hfs of the radical anion [4-$O_2NC_6H_4C(H)$=NOH]$^{-\bullet}$ in DMF were: a(N) = 7.3 G, a(2H) = 3.0 G, a(2H) = 1.0 G, a(1H) = 1.0, a(1H) = 0.3 G, a(N) = 2.0 G at 300 K [37] and hence this possibility can be ruled out. The species generated from **6a** remains unidentified.

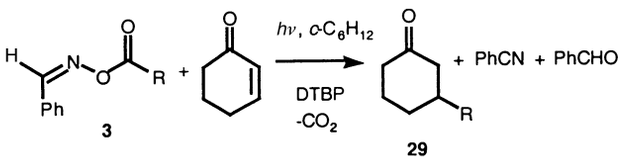
The parameters of the iminyl radicals deserve some comment. It can be seen from Table 1 (footnotes) that the hfs of the iminyl hydrogens increase as from **13** to **14** to **15**, *i.e.* as the degree of ring methoxy substitution increases. Most likely this effect is steric in origin. The extremely large iminyl H-hfs is caused by the excellent overlap of the σ-orbital containing the unpaired electron, and the C–H bond σ-orbital. Structures **28a** and **28b** illustrate that there will be steric interaction between the methoxy groups and this iminyl hydrogen that will result in the phenyl ring twisting out of the plane of the imine group, hence reducing the delocalisation into the ring and increasing the amount of electron density in the aldiminyl system.



Interestingly, the MAP photosensitised reaction of benzophenone oxime ester **8** led to slightly different results. The EPR spectra in the temperature range 230–300 K showed the presence of the iminyl radical Ph_2C=N$^{\bullet}$ and the *n*-octyl radical, as expected by analogy with aldoxime esters. However, a significant amount of the iminoxyl radical **19** (Table 1) accompanied these species, suggesting that O–C bond dissociation accompanied N–O bond cleavage for this type of ketoxime ester (Scheme 3). The only instance we observed of iminoxyl (**19**) formation with an aldoxime ester was from the MAP photosensitised reaction of **4d** which gave a very minor amount of the corresponding iminoxyl [a(N) = 32.0 G at 245 K, with some unresolved fine structure]. Forrester *et al.* observed iminoxyl radical formation in similar experiments, caused by photolytic cleavage of the C–O bond.[38] Hence it appears that O–C bond fission (Scheme 3) can compete with N–O bond cleavage for ketoxime esters.

Investigation of the photo-induced reactions of oxime esters by product analysis

Initial intermolecular reactions were performed with cyclohex-2-enone as a radical acceptor. An oxime ester and cyclohex-2-enone were irradiated for 2–3 hours in neat DTBP, or in DTBP in cyclohexane, using a medium pressure mercury lamp. Product analysis by GC–MS indicated that 3-alkylcyclohexanone adducts **29** were indeed formed from **3a** and **3b**, together with benzonitrile and benzaldehyde, produced from the iminyl

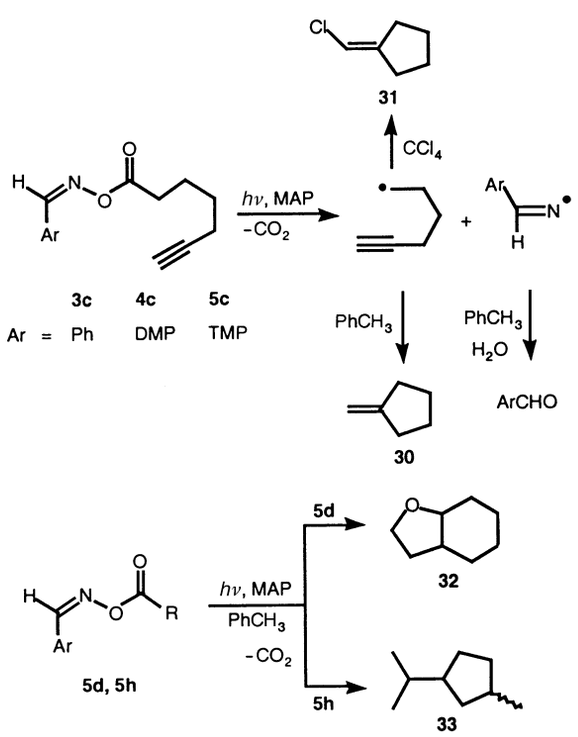


Scheme 6

radical (Scheme 6). Use of benzoyl peroxide as a thermal initiator resulted in a yield of zero.

The reactions of oxime esters with different aromatic groups were now investigated under the same reaction conditions. Product analyses of the cyclisation reactions of **3d**–**7d** revealed that some 2-oxabicyclo[4.3.0]nonane was formed from all esters except the pentafluorobenzaldoxime derivatives. The highest yields (approximated from peak areas) were obtained from the 2,4-dimethoxy derivatives, while the *p*-nitrobenzaldoxime derivatives showed the poorest results, pentafluoro derivatives excepted. Further work concentrated on benzaldoxime, 2,4-dimethoxybenzaldoxime and 2,4,6-trimethoxybenzaldoxime derivatives.

Solutions of individual oxime esters (*ca.* 0.13 mol dm^{-3}) in a hydrogen donor solvent ($PhCH_3$, DCM) were photolysed with light from a 400 W medium pressure Hg lamp for *ca.* 3 h. Table 4 shows that for **3c** yields of the cyclised product, methylenecyclopentane (**30**) were low, but improved on inclusion of photosensitiser. Best yields of **30** were, however, obtained from the dimethoxy oxime ester **4c** when photosensitiser was included. The bicyclic ether **32** was obtained in good yield from photolysis of the trimethoxy oxime ester **5d**, but the yield of 1-isopropyl-3-methylcyclopentane (**33**) from **5h** was moderate,



Scheme 7

possibly because of poor hydrogen donation to the tertiary cyclised radical by the solvent. No uncyclised products from direct reduction of the initial unsaturated alkyl radicals were detected. This is an advantage in that by-products are minimised, but indicated that, as expected, hydrogen donation was slow. The main products derived from the iminyl radicals were the corresponding aldehydes, probably formed from intermediate imines, ArCH=NH, which are known to be highly susceptible to hydrolysis. GC–MS analysis indicated that reactions were clean, but the volatility of the products, coupled with limitations of the scale of reaction, meant that attempts to isolate products were not very successful. However, bicyclic ether **32** was isolated from reaction of **5d** in 12% yield (72% by NMR, Table 4). The reaction was also performed in diethyl ether as a volatile hydrogen donor, and this afforded 21% of bicyclic ester **32**.

Table 4 Ring closure from photochemical reactions of oxime ethers

Oxime ether	Ar[a]	Solvent	MAP	Product (%)[b]
3c	Ph	$PhCH_3$	None	**30** (6)
3c	Ph	$PhCH_3$	1 eq.	**30** (28)
4c	DMP	$PhCH_3$	None	**30** (39)
4c	DMP	$PhCH_3$	1 eq.	**30** (77)
5c	TMP	CCl_4	1 eq.	**31** (62)
5h	TMP	$PhCH_3$	1 eq.	**33** (34)
5d	TMP	DCM	1 eq.	**32** (72)

[a] DMP = 2,4-dimethoxyphenyl, TMP = 2,4,6-trimethoxyphenyl. [b] Yields determined by NMR.

An advantage of the method is that halogen-donor solvents can also be used for the preparation of functionalised rings. The reactions were found to be awkward to perform however. Illumination of a solution of any oxime ester in carbon tetrachloride in a quartz tube resulted in the formation of a cloudy yellow mixture. Best results were obtained when extremely low concentrations were used. *O*-Heptanoyl 2,4-dimethoxybenzaldoxime **4g** was converted (in the presence of MAP) into 1-chlorohexane in 44% yield (77% based on reacted starting material). Similarly, photolysis of a dilute solution of *O*-hept-6-ynoyl 2,4,6-trimethoxybenzaldoxime **5c** in carbon tetrachloride resulted in the formation of chloromethylenecyclopentane **31** in an approximate yield of 62% (Scheme 7).

Conclusions

The photolyses of aldoxime esters, containing a considerable range of alkyl groups, lead to cleavage of their N–O bonds and formation of aryliminyl and alkyl radicals. The process was found to be favoured by MAP as a photosensitiser and by methoxy substituents in the aryl rings. 4-Nitro- and pentafluoro-substitution of the aryl rings were, on the other hand, deleterious. The intermediate iminyl radicals, together with primary, secondary and tertiary alkyl radicals were characterised by 9 GHz EPR spectroscopy. The large doublet H-hfs and comparatively few lines of the methaniminyl radicals **13**–**15** provided a 'window' of *ca.* 60 G in the centre of the EPR spectrum that minimised overlap with the co-radical. Furthermore, the iminyl spectra acted as useful standards with known *g*-factors so that spectral analysis of the co-radical was facilitated. Thus, these oxime esters constitute a convenient new class of radical precursors suitable for spectroscopic studies. Photolyses of oxime esters, which were potentially precursors of σ-radicals, showed the expected iminyl radicals. The corresponding σ-radicals (cyclopropyl, CF_3, CCl_3) were probably also formed but were too reactive for direct EPR spectroscopic detection. Photosensitised reaction of benzophenone oxime *O*-nonanoyl ester produced the diphenylmethaniminoxyl, as well as the expected *n*-octyl and iminyl radicals. This indicated that O–C bond scission accompanied O–N scission for this ketoxime ester.

At higher temperatures the C-centred radicals added to the starting oxime esters to produce alkoxyaminyl radicals that were also spectroscopically detected in some cases. No evidence for abstraction of the iminyl hydrogen by *tert*-butoxyl radicals was obtained. Instead, the *t*-BuO$^{\bullet}$ radicals added to the C=N double bonds of the oxime ethers. Similarly, chlorine

abstraction from alkylbenzohydroximoyl chlorides by trimethyltin radicals did not take place. The stannyl radicals added to the iminyl unit affording, after oxidation, alkoxyaminoxyls.

Preparative scale experiments with oxime esters containing suitably unsaturated alkyl groups showed that good yields of cyclised products could be obtained in the presence of the photosensitiser. This process constitutes a general method by which carboxylic acids or acid chlorides can be converted into alkyl radicals and hence to cyclised derivatives. It is metal free and, as such, offers a 'green' alternative to current radical processes mediated by organotin compounds.

Experimental

^{1}H NMR spectra were recorded at 200 or 300 MHz and ^{13}C NMR spectra at 75 MHz, in $CDCl_3$ solutions with tetramethylsilane ($\delta_H = \delta_C = 0$) as reference. Coupling constants are expressed in Hz. EI mass spectra were obtained with 70 eV electron impact ionisation and CI spectra were obtained with isobutane as target gas on a VG autospec spectrometer. GC–MS analyses were run on a Finnigan Incos 50 quadrupole instrument coupled to a Hewlett Packard HP 5890 chromatograph fitted with a 25 m HP 17 capillary column (50% phenyl methyl silicone). For the calculation of yields from GC data, the detector response was calibrated with known amounts of authentic materials (or close analogues) and *n*-dodecane, or *n*-heptane was added as a standard. EPR spectra were obtained with a Bruker EMX 10/12 spectrometer operating at 9.5 GHz with 100 kHz modulation. Samples of the substrate (*ca*. 40 mg) and *p*-methoxyacetophenone (when required) in di-*tert*-butyl peroxide (0.5 cm^3) or in *tert*-butylbenzene (0.5 cm^3) were de-aerated by bubbling nitrogen for 20 min and photolysed in the resonant cavity by light from a 500 W super pressure mercury arc lamp. For reactions performed in cyclopropane, the solution was degassed on a vacuum line using the freeze–pump–thaw technique, and the tube flame sealed. The *O*-alkylbenzohydroximoyl chloride (~0.03 g) and hexamethylditin (~0.03 g) were dissolved in *tert*-butylbenzene (300 μl) and the mixtures de-aerated by passing a stream of nitrogen through them. In all cases where spectra were obtained, hfs were assigned with the aid of computer simulation using the Bruker Simfonia software package.

Ether refers to diethyl ether. THF and ether were distilled under nitrogen from sodium benzophenone ketyl prior to use. Where dry DCM was used, it was distilled over CaH_2. Petroleum ether (PE) refers to the fraction boiling between 40 and 60 °C. Other organic compounds were used as received. Column chromatography was performed using BDH silica gel (40–63 μm).

syn-Benzaldoxime, *p*-nitrobenzaldoxime, pentafluorobenzaldoxime, 2,4-dimethoxybenzaldoxime, 2,4,6-trimethoxybenzaldoxime, and di-*tert*-butyl peroxyoxalate were prepared as described previously.[26] Benzophenone oxime,[9] 3-(cyclohex-2-enyloxy)propan-1-ol **9**,[39] 3-(cyclohex-2-enyloxy)propionitrile **10**,[18,19] 3-(cyclohex-2-enyloxy)propionic acid **11**[20] and benzohydroximoyl chloride **25**,[30] were prepared as described in the literature.

Swern oxidation of 3-(cyclohex-2-enyloxy)propan-1-ol[16]

To a three-necked flask, fitted with two pressure equalised dropping funnels and a drying tube, containing oxalyl chloride (1.0 cm^3; 11 mmol) in DCM (25 cm^3) was added DMSO (1.7 cm^3; 22 mmol) in DCM (5 cm^3). The mixture was stirred for 2 min, then 3-(cyclohex-2-enyloxy)propan-1-ol (1.56 g; 10 mmol) in DCM (10 cm^3) was added and the mixture cooled to −75 °C and stirred for a further 15 min. Triethylamine (7.0 cm^3; 50 mmol) was added, and the mixture was stirred for a further 5 min, then allowed to warm to room temperature. Water (50 cm^3) was added, and the mixture extracted with DCM (2 × 50 cm^3). The combined organic layers were washed with brine (100 cm^3), 1% HCl (70 cm^3), H_2O (70 cm^3), a 5% aqueous solution of Na_2CO_3 (100 cm^3) and H_2O (100 cm^3), then dried ($MgSO_4$) and concentrated. Distillation yielded 3-(cyclohex-2-enyloxy)propanal (3.00 g; 65%), bp 42–44 °C/0.5 mmHg. δ_H (200 MHz) 1.50–2.10 (6H, m, cycloalkyl CH_2s), 2.63–2.74 (2H, m, CH_2CO), 3.78–3.95 (3H, m, R_2CHO and OCH_2), 5.70–5.95 (2H, m, CH=CH), 9.81 (1H, s, CHO).

Typical syntheses of oxime esters

Method A. To a stirred mixture of oxime (20 mmol) and triethylamine (20 mmol) in DCM (100 cm^3) at 0 °C was added the acid chloride (20 mmol) in DCM (20 cm^3) dropwise. The mixture was stirred for 20 min, then 2 M HCl was added (100 cm^3). The organic layer was washed with saturated aqueous sodium bicarbonate (3 × 100 cm^3) and brine (1 × 100 cm^3), then dried ($MgSO_4$), and concentrated. Column chromatography on silica gel (PE–EtOAc or PE–DCM) yielded pure product.

Method B. The carboxylic acid (2.54 mmol), oxime (2.54 mmol) and DMAP (0.02 g) were stirred in DCM (9 cm^3) at 0 °C. DCC (2.54 mmol) was added, and the mixture stirred at 0 °C for twelve hours. The mixture was filtered, and the filtrate concentrated. Recrystallisation or column chromatography yielded pure product.

***O*-Trimethylacetyl benzaldoxime 3a.**[40] Prepared from benzaldoxime and trimethylacetyl chloride according to method A, to give *O*-trimethylacetyl benzaldoxime as white crystals (3.06 g, 79%) after column chromatography (PE–DCM), mp 38.5–40 °C. δ_H 1.32 (9H, s, $C(CH_3)_3$), 7.44–7.50 (3H, m, ArH), 7.75 (2H, d, J = 6.2 Hz, ArH), 8.38 (1H, s, PhCH=N-). δ_C 27.3, 38.5, 128.6, 129.1, 130.5, 131.8, 156.5, 175.6 (Found: M$^+$, 231.1263. $C_{12}H_{15}NO_2$ requires *M*, 231.1259).

***O*-Cyclohexylcarbonyl benzaldoxime 3b.** Prepared from benzaldoxime and cyclohexylcarbonyl chloride according to method A to give *O*-cyclohexylcarbonyl benzaldoxime (1.11 g, 48%) as white crystals after column chromatography (PE–DCM), mp 78–79 °C. δ_H 1.25–1.35 (11H, m), 7.39–7.47 (3H, m, ArH), 7.73–7.76 (2H, m, ArH), 8.36 (1H, s, PhCH=N-). δ_C 25.5, 25.7, 29.0, 42.1, 128.6, 129.1, 130.5, 131.8, 156.3, 173.5 (Found: M$^+$, 205.1109. $C_{12}H_{15}NO_2$ requires *M*, 205.1103).

***O*-Hept-6-ynoyl benzaldoxime 3c.** To DCM (20 cm^3) was added hept-6-ynoic acid (0.25 g; 2 mmol) and oxalyl chloride (0.30 g; 2.4 mmol). The mixture was stirred overnight, and the solvent evaporated. The product was used directly in the synthesis of **3c** (method A) which was formed as white crystals (0.23 g from acid; 50%) after column chromatography (PE–DCM), mp 59.5–60.5 °C. δ_H 1.6–1.7 (2H, tt, J_1 = 7.2, J_2 = 7.7 Hz, CH_2), 1.8–1.9 (2H, tt, J_1 = 7.8, J_2 = 7.4 Hz, CH_2), 1.96 (1H, t, J = 2.6 Hz, CCH), 2.21–2.28 (2H, td, J_1 = 2.6, J_2 = 6.6 Hz, CH_2CH_2CCH), 2.48–2.54 (2H, t, J = 7.4 Hz, $COCH_2$-), 7.40–7.50 (3H, m, ArH), 7.70–7.75 (2H, m, ArH), 8.35 (1H, s, PhCH=N-). δ_C 18.2, 23.9, 27.8, 32.3, 68.8, 84.0, 128.6, 129.1, 130.4, 131.9, 156.3, 171.2 (Found: M$^+$, 229.1098. $C_{14}H_{15}NO_2$ requires *M*, 229.1102).

***O*-[3-(Cyclohex-2-enyloxy)propionyl] benzaldoxime 3d.** Prepared from benzaldoxime and 3-(cyclohex-2-enyloxy)propionic acid (3.76 mmol) according to method B to give **3d** (0.46 g; 48%) as a colourless oil after column chromatography (PE–DCM). δ_H 1.51–2.05 (6H, m, ring Hs), 2.76 (2H, t, J = 6.6 Hz, -OCH_2-), 3.79–3.95 (3H, m, OCR_2H-, CO_2CH_2), 5.75–5.89 (2H, m, -HC=CH-), 7.39–7.51 (3H, m, ArH), 7.72–7.75 (2H, m, ArH), 8.37 (1H, s, -CH=N-). δ_C 19.1, 25.2, 28.1, 34.2, 63.3, 73.3, 127.7, 128.5, 129.0, 130.3, 131.2, 131.8, 155.3, 169.6 (Found: M$^+$, 273.1371. $C_{16}H_{19}NO_3$ requires *M*, 273.1365).

***O*-Trimethylacetyl 4-nitrobenzaldoxime 6a.**[40] Prepared from 4-nitrobenzaldoxime and pivaloyl chloride according to method A to give *O*-trimethylacetyl *p*-nitrobenzaldoxime (1.92 g; 77%) as pale yellow crystals after recrystallisation (CH_3CN), mp 167.5–168.0 °C (lit.[41] 170–172 °C). δ_H 1.34 (9H, s, $C(CH_3)_3$), 7.95 (2H, dt, $J_1 = 2.2$, $J_2 = 9.1$ Hz, ArH), 8.29 (2H, dt, $J_1 = 2.2$, $J_2 = 8.8$ Hz, ArH), 8.48 (1H, s, CH=N). δ_C 27.1, 38.4, 124.2, 129.2, 136.4, 149.7, 154.0, 175.1.

***O*-[3-(Cyclohex-2-enyloxy)propionyl] 4-nitrobenzaldoxime 6d.** Prepared from 4-nitrobenzaldoxime and 3-(cyclohex-2-enyloxy)propionic acid on a 5.12 mmol scale according to method B to give *O*-[3-(cyclohex-2-enyloxy)propionyl] 4-nitrobenzaldoxime (1.24 g; 80%) as yellow crystals after column chromatography (PE–DCM), mp 66–68 °C. δ_H 1.52–2.02 (6H, m, ring Hs), 2.78 (2H, t, $J = 6.5$ Hz, $-OCH_2-$), 3.80–3.95 (3H, m, OCR_2H-, CO_2CH_2), 5.74–5.90 (2H, m, -HC=CH-), 7.93 (2H, d, $J = 8.8$ Hz, ArH), 8.30 (2H, d, $J = 8.8$ Hz, ArH), 8.46 (1H, s, -CH=N-). δ_C 19.2, 25.2, 28.2, 34.1, 63.2, 73.5, 124.3, 127.6, 129.4, 131.5, 136.4, 149.8, 154.0, 169.1 (Found: C, 60.7; H, 5.9; N, 8.9%. Calc. for $C_{16}H_{18}N_2O_5$: C, 60.4; H, 5.7; N, 8.8%).

***O*-Trimethylacetyl pentafluorobenzaldoxime 7a.** Prepared from pentafluorobenzaldoxime and pivaloyl chloride according to method A to give **7a** as white crystals (2.05 g; 73%) after column chromatography (DCM), mp 53–55 °C. δ_C 1.35 (9H, s, $-C(CH_3)_3$), 8.5 (1H, s, CH=N), δ_C 27.1, 38.44, 105.9–106.3 (m), 136.0–136.5 (m), 139.4–139.8 (m), 140.2, 141.0–141.3 (m), 143.6–143.9 (m), 144.4–144.9 (m), 145.4, 147.1–147.4 (m), 174.4.

***O*-[3-(Cyclohex-2-enyloxy)propionyl] pentafluorobenzaldoxime 7d.** Prepared from pentafluorobenzaldoxime and 3-(cyclohex-2-enyloxy)propionic acid according to method B to give **7d** (0.58 g; 62%) as an oil after column chromatography (DCM). δ_H 1.51–2.05 (6H, m, ring CH_2s), 2.79 (2H, t, $J = 6.4$ Hz, CH_2O), 3.79–3.94 (3H, m, OCR_2H-, CO_2CH_2), 5.73–5.89 (2H, m, HC=CH), 8.49 (1H, s, -CH=N). δ_C 19.2, 25.3, 28.2, 34.0, 63.2, 73.5, 127.7, 131.5, 145.5, 168.9 (Found: C, 52.9; H, 3.8; N, 3.9%. Calc. for $C_{16}H_{14}F_5NO_3$: C, 52.9; H, 3.9; N, 3.9%).

***O*-Trimethylacetyl 2,4-dimethoxybenzaldoxime 4a.**[13] Prepared from 2,4-dimethoxybenzaldoxime (2.5 mmol) and pivaloyl chloride according to method A, and purified by column chromatography (DCM–PE) to give a colourless oil, which slowly crystallised, and could be recrystallised from toluene–hexane to give pure *O*-trimethylacetyl 2,4-dimethoxybenzaldoxime (0.41 g; 62%) as white crystals, mp 66–67 °C (lit.[13] 89 °C). δ_H 1.32 (9H, s, $-C(CH_3)_3$), 3.82 (6H, s, -OMe), 6.56 (1H, s, ArH), 6.88 (2H, d, $J = 2.2$ Hz, ArH), 8.30 (1H, s, -CH=N) (Found: C, 63.5; H, 7.3; N, 5.4%. Calc. for $C_{14}H_{19}NO_4$: C, 63.4; H, 7.2; N, 5.3%).

***O*-Cyclohexanecarbonyl 2,4-dimethoxybenzaldoxime 4b.** Prepared from 2,4-dimethoxybenzaldoxime (2.5 mmol) and cyclohexanecarboxylic acid according to method B to give *O*-cyclohexanecarbonyl 2,4-dimethoxybenzaldoxime (0.58 g; 78%) as white crystals after recrystallisation (toluene), mp 91–93 °C. δ_H 1.28–2.01 (10H, m, alkyl Hs), 2.41–2.49 (1H, m, $-CHR_2$), 3.84 (3H, s, OMe), 3.84 (3H, s, OMe), 6.44 (1H, d, $J = 2.2$ Hz, ArH), 6.52 (1H, dd, $J_1 = 2.5$, $J_2 = 8.8$ Hz, ArH), 7.94 (1H, d, $J = 8.5$ Hz, ArH), 8.68 (1H, s, -CH=N-). δ_C 25.4, 25.7, 29.0, 42.2, 55.5, 55.6, 98.2, 105.6, 111.5, 128.9, 151.9, 159.9, 163.9, 173.6 (Found: C, 66.7; H, 6.8; N, 4.9%. Calc. for $C_{16}H_{19}NO_4$: C, 66.4; H, 6.6; N, 4.8%).

***O*-Hept-6-ynoyl 2,4-dimethoxybenzaldoxime 4c.** Prepared from 2,4-dimethoxybenzaldoxime and hept-6-ynoic acid according to method B to give *O*-hept-6-ynoyl 2,4-dimethoxybenzaldoxime (0.64 g; 87%) as white crystals after recrystallisation (toluene), mp 101–103 °C. δ_H 1.65 (2H, m, $-CH_2-$), 1.81–1.90 (2H, m, $-CH_2-$), 1.96 (1H, t, $J = 2.6$ Hz, CCH), 2.21–2.28 (2H, td, $J_1 = 2.6$, $J_2 = 7.0$ Hz, CH_2CH_2CCH), 2.49 (2H, t, $J = 7.4$ Hz, $COCH_2-$), 3.85 (3H, s, -OMe), 3.85 (3H, s, -OMe), 6.43 (1H, d, $J = 2.3$ Hz, ArH), 6.52 (1H, m, ArH), 7.92 (1H, d, $J = 8.7$ Hz, ArH), 8.68 (1H, s, PhCH=N-). δ_C 18.1, 23.9, 27.8, 32.4, 55.5, 55.6, 68.7, 83.9, 98.2, 105.6, 111.3, 128.6, 151.9, 160.0, 164.0, 171.2 (Found: M^+, 289.1309. $C_{16}H_{19}NO_4$ requires *M*, 289.1314).

***O*-[3-(Cyclohex-2-enyloxy)propionyl] 2,4-dimethoxybenzaldoxime 4d.** Prepared from 2,4-dimethoxybenzaldoxime and 3-(cyclohex-2-enyloxy)propionic acid according to method B to give *O*-[3-(cyclohex-2-enyloxy)propionyl] 2,4-dimethoxybenzaldoxime (0.68 g; 81%) as white crystals after column chromatography (PE–EtOAc), mp 60.0–61.0 °C. δ_H 1.53–2.04 (6H, m, ring Hs), 2.76 (2H, t, $J = 6.6$ Hz, $-OCH_2-$), 3.78–3.94 (9H, m, OCR_2H-, CO_2CH_2, $2 \times CH_3O-$), 5.74–5.88 (2H, m, -HC=CH-), 6.56 (1H, t, $J = 2.2$ Hz, ArH), 6.85 (2H, d, $J = 2.2$ Hz, ArH), 8.28 (1H, s, -CH=N-). δ_C 19.2, 25.2, 28.2, 34.3, 55.7, 63.3, 73.4, 104.6, 106.3, 127.7, 131.3, 132.1, 156.6, 161.3, 169.6 (Found: C, 64.92; H, 7.13; N, 4.43%. Calc. for $C_{18}H_{23}NO_5$: C, 64.85; H, 6.95; N, 4.20%).

***O*-Vinylacetyl 2,4-dimethoxybenzaldoxime 4e.** Prepared from vinylacetic acid (2.54 mmol) and dimethoxybenzaldoxime according to method B to give *O*-vinylacetyl 2,4-dimethoxybenzaldoxime (0.56 g; 89%) as white crystals after recrystallisation (toluene), mp 64.5–65.5 °C. δ_H 3.25 (2H, m, $-CH_2-$), 3.85 (6H, s, 2-OCH_3), 5.21–5.28 (2H, m, $=CH_2$), 5.96–6.05 (1H, m, -CH=), 6.44 (1H, d, $J = 2.2$ Hz, ArH), 6.52 (1H, dd, $J_1 = 2.2$, $J_2 = 8.8$ Hz, ArH), 7.92 (1H, d, $J = 8.8$ Hz, ArH), 8.68 (1H, s, -CH=N-). δ_C 38.0, 55.6, 55.7, 98.4, 105.9, 111.5, 119.2, 129.1, 130.0, 152.4, 160.3, 164.3, 169.6 (Found: M^+, 249.1008. $C_{13}H_{15}NO_4$ requires *M*, 249.1001).

***O*-Isobutyryl 2,4-dimethoxybenzaldoxime 4f.** Prepared from isobutyric acid and 2,4-dimethoxybenzaldoxime according to method B to give *O*-isobutyryl 2,4-dimethoxybenzaldoxime (0.58 g; 91%) as white crystals after recrystallisation (toluene), mp 67.5–68.5 °C. δ_H 1.15–1.28 (6H, d, $J = 6.8$ Hz, $2CH_3$), 2.66–2.72 (1H, m, $-CH(CH_3)_2$), 3.85 (6H, s, 2-OCH_3), 6.44 (1H, d, $J = 2.2$ Hz, ArH), 6.52 (1H, dd, $J_1 = 2.2$, $J_2 = 8.8$ Hz), 7.94 (1H, d, $J = 8.8$ Hz), 8.68 (1H, s, -CH=N-). δ_C 19.0, 32.9, 55.5, 55.6, 98.2, 105.6, 111.4, 128.9, 152.0, 159.9, 163.9, 174.7 (Found: C, 62.5; H, 7.1; N, 5.8%. Calc. for $C_{13}H_{17}NO_4$: C, 62.1; H, 6.8; N, 5.6%).

***O*-Heptanoyl 2,4-dimethoxybenzaldoxime 4g.** Prepared from 2,4-dimethoxybenzaldoxime and heptanoic acid according to method B to give *O*-heptanoyl 2,4-dimethoxybenzaldoxime (0.41 g; 55%) as white crystals after recrystallisation (toluene), mp 53.0–57.0 °C. δ_H 0.89 (3H, t, $J = 6.6$ Hz, CH_3), 1.31–1.38 (4H, m, $2 \times CH_2$), 1.72 (2H, m, $-CH_2-$), 2.44 (2H, t, $J = 7.6$ Hz, $CH_2C(O)$), 3.85 (6H, s, $2 \times$ OMe), 6.44 (1H, d, $J = 2.2$ Hz, ArH), 6.52 (1H, dd, $J_1 = 2.5$, $J_2 = 8.8$ Hz, ArH), 7.93 (1H, d, $J = 8.8$ Hz, ArH), 8.67 (1H, s, PhCH=N-). δ_C 14.0, 22.5, 24.9, 28.9, 31.4, 33.0, 55.5, 55.6, 98.2, 105.6, 111.4, 128.8, 151.8, 159.9, 163.9, 171.6 (Found: M^+, 293.1635. $C_{16}H_{23}NO_4$ requires *M*, 293.1627).

***O*-[2,6-Dimethylhept-5-enecarbonyl] 2,4-dimethoxybenzaldoxime 4h.** Prepared from citronellic acid and 2,4-dimethoxybenzaldoxime on a 5.12 mmol scale according to method B to give *O*-[2,6-dimethylhept-5-enecarbonyl] 2,4-dimethoxybenzaldoxime (1.19 g; 70%) as a colourless oil. δ_H 1.02 (3H, d, $J = 6.6$ Hz, $-CH(CH_3)-$), 1.22–1.61 (4H, m, $2CH_2$), 1.61 (3H, s, $=C(CH_3)$), 1.68 (3H, s, $=C(CH_3)$), 1.95–2.11 (1H, m, $-CH(CH_3)-$), 2.21–2.49 (2H, m, $C(O)CH_2-$), 3.85 (6H, s, 2OMe), 5.11 (1H, t, $J = 7.1$ Hz, -CH=), 6.44 (1H, d, $J = 2.2$ Hz,

ArH), 6.52 (1H, dd, $J_1 = 2.2$, $J_2 = 8.8$ Hz, ArH), 7.94 (1H, d, $J = 8.8$ Hz, ArH), 8.67 (1H, s, -CH=N-). δ_C 17.7, 19.7, 25.5, 25.8, 30.2, 36.9, 40.4, 55.6, 55.7, 98.4, 105.8, 111.7, 124.5, 129.1, 131.8, 152.1, 160.3, 164.2, 171.2 (Found: M^+, 333.1953. $C_{19}H_{27}NO_4$ requires *M*, 333.1940).

***O*-Trimethylacetyl 2,4,6-trimethoxybenzaldoxime 5a.** Prepared from 2,4,6-trimethoxybenzaldoxime and trimethylacetic acid according to method B to give *O*-trimethylacetyl 2,4,6-trimethoxybenzaldoxime (0.72 g; 96%) as white crystals after recrystallisation (toluene–hexane), mp 87.5–89 °C. δ_H 1.30 (9H, s, -C(CH_3)$_3$), 3.86 (3H, s, *p*-OMe), 3.89 (6H, s, *o*-OMe), 6.12 (2H, s, ArH), 8.75 (1H, s, CH=N). δ_C 27.3, 38.3, 55.8, 90.5, 90.6, 100.7, 151.8, 152.0, 161.4, 164.2, 175.8 (Found: M^+, 295.1414. $C_{19}H_{27}NO_4$ requires *M*, 295.1420).

***O*-Hept-6-ynoyl 2,4,6-trimethoxybenzaldoxime 5c.** Prepared from 2,4,6-trimethoxybenzaldoxime and hept-6-ynoic acid according to method B to give hept-6-ynoyl 2,4,6-trimethoxybenzaldoxime (0.65 g; 80%) as white crystals after recrystallisation (DCM–hexane), mp 94.0–95.0 °C. δ_H 1.61–1.66 (2H, m, -CH_2), 1.82–1.88 (2H, m, -CH_2), 1.95 (1H, t, $J = 2.6$ Hz, C≡CH), 2.24 (2H, dt, $J_1 = 2.6$, $J_2 = 6.8$ Hz, CH_2C≡CH), 2.48 (2H, t, $J = 7.4$ Hz, CH_2), 3.85 (3H, s, -OMe), 3.88 (6H, s, 2OMe), 6.12 (2H, s, ArH), 8.74 (1H, s, -CH=N-). δ_C 18.2, 24.0, 27.9, 32.5, 55.5, 56.2, 68.7, 84.1, 90.7, 100.7, 152.0, 161.5, 164.4, 171.6 (Found: C, 63.6; H, 6.7; N, 4.5%. Calc. for $C_{17}H_{21}NO_5$: C, 63.9; H, 6.6; N, 4.4%).

***O*-[3-(Cyclohex-2-enyloxy)propionyl] 2,4,6-trimethoxybenzaldoxime 5d.** Prepared from 2,4,6-trimethoxybenzaldoxime and 3-(cyclohex-2-enyloxy)propionic acid (3.78 mmol) according to method B to give *O*-[3-(cyclohexenyloxy)propionyl] 2,4,6-trimethoxybenzaldoxime (0.61 g; 44%) as white crystals after chromatography (PE–DCM) and two recrystallisations (DCM–THF), mp 83.0–85.5 °C. δ_H 1.53–2.01 (6H, m, ring Hs), 2.76 (2H, t, $J = 6.9$ Hz, -OCH_2-), 3.78–3.91 (9H, m, OCR_2H-, CO_2CH_2, 2 × CH_3O-), 5.75–5.87 (2H, m, -HC=CH-), 6.12 (2H, s, ArH), 8.74 (1H, s, -CH=N-). δ_C 19.2, 25.2, 28.2, 34.3, 55.4, 56.0, 63.4, 73.2, 90.5, 100.4, 127.7, 130.9, 151.9, 161.2, 164.1, 169.6 (Found: C, 62.9; H, 6.9; N, 3.9%. Calc. for $C_{19}H_{25}NO_6$: C, 62.8; H, 6.9; N, 4.1%).

***O*-(2,6-Dimethylhept-5-enecarbonyl) 2,4,6-trimethoxybenzaldoxime 5h.** Prepared from citronellic acid and 2,4,6-trimethoxybenzaldoxime according to method B to give *O*-(2,6-dimethylhept-5-enecarbonyl) 2,4,6-trimethoxybenzaldoxime as white crystals (0.54 g; 63%) after recrystallisation (DCM–hexane), mp 47.0–48.0 °C. δ_H 1.02 (3H, d, $J = 6.6$ Hz, -CH-(CH_3)), 1.22–1.61 (4H, m, 2CH_2), 1.61 (3H, s, =C(CH_3)), 1.68 (3H, s, =C(CH_3)), 1.97–2.14 (1H, m, -CH(CH_3)-), 2.21–2.49 (2H, m, C(O)CH_2-), 3.85 (3H, s, -OMe), 3.88 (6H, s, 2 OMe), 5.11 (1H, m, -CH=), 6.44 (1H, d, $J = 2.2$ Hz, ArH), 6.12 (2H, ArH), 8.74 (1H, s, -CH=N-). δ_C 17.7, 19.7, 25.5, 25.8, 30.1, 36.9, 40.5, 55.5, 56.2, 90.7, 100.8, 124.6, 131.7, 151.9, 161.1, 164.3, 171.3 (Found: C, 66.3; H, 8.2; N, 4.0%. Calc. for $C_{20}H_{29}NO_5$: C, 66.1; H, 8.0; N, 3.9%).

***O*-Valeryl 2,4,6-trimethoxybenzaldoxime 5i.** Prepared from 2,4,6-trimethoxybenzaldoxime (2 mmol) and valeryl chloride according to method A to give *O*-valeryl 2,4,6-trimethoxybenzaldoxime (0.38 g; 65%), as white crystals after column chromatography (PE–EtOAc), and recrystallisation (toluene–hexane), mp 75–76.5 °C. δ_H 0.93 (3H, t, $J = 7.1$ Hz, -CH_3), 1.40 (2H, m, CH_2CH_3), 1.73 (2H, m, -CH_2), 2.40–2.65 (2H, m, -CH_2), 3.85 (3H, s, *p*-OMe), 3.88 (6H, s, *o*-OMe), 6.12 (2H, s, ArH), 8.74 (1H, s, CH=N). δ_C 13.7, 22.4, 27.0, 32.8, 55.5, 56.2, 90.7, 100.8, 151.8, 161.5, 164.3, 172.0 (Found: C, 61.1; H, 7.7; N, 4.7%. Calc. for $C_{15}H_{21}NO_5$: C, 61.0; H, 7.2; N, 4.7%).

***O*-Cyclopropylcarbonyl 2,4,6-trimethoxybenzaldoxime 5j.** Prepared from cyclopropanecarboxylic acid and 2,4,6-trimethoxybenzaldoxime according to method B to give *O*-cyclopropylcarbonyl 2,4,6-trimethoxybenzaldoxime (0.63 g; 89%) as white crystals after recrystallisation (toluene), mp 113.5–115 °C. δ_H 0.89–0.95 (2H, m, cyclopropyl Hs), 1.11–1.16 (2H, m, cyclopropyl Hs), 1.70–1.81 (1H, m, -CH(CH_2)$_2$), 3.84 (3H, s, *p*-OCH_3), 3.88 (6H, s, *o*-OCH_3), 6.12 (2H, s, ArH), 8.77 (1H, s, -CH=N-). δ_C 8.6, 11.5, 55.4, 56.1, 90.5, 100.6, 151.1, 161.2, 164.0, 172.9 (Found: C, 60.5; H, 6.2; N, 5.2%. Calc. for $C_{14}H_{17}NO_5$: C, 60.2; H, 6.1; N, 5.0%).

***O*-Trichloromethylcarbonyl 2,4,6-trimethoxybenzaldoxime 5k.** Prepared from trichloroacetic acid and 2,4,6-trimethoxybenzaldoxime according to method B. Product decomposed very rapidly. δ_H (200 MHz) 3.87 (3H, s, *p*-OCH_3), 3.91 (6H, s, *o*-OCH_3), 6.13 (2H, s, ArH), 8.93 (1H, s, -CH=N-).

***O*-Trifluoromethylcarbonyl 2,4,6-trimethoxybenzaldoxime 5l.** Prepared from trifluoroacetic acid and 2,4,6-trimethoxybenzaldoxime according to method B to give *O*-trifluoromethyl 2,4,6-trimethoxybenzaldoxime (90% crude yield). δ_H 3.87 (3H, s, *p*-OCH_3), 3.91 (6H, s, *o*-OCH_3), 6.13 (2H, s, ArH), 8.91 (1H, s, -CH=N-) (Found: C, 46.4; H, 4.4; N, 5.2%. Calc. for $C_{12}H_{12}F_3NO_5$: C, 46.9; H, 3.9; N, 4.6%).

***O*-Nonanoyl benzophenone oxime 8.** Prepared from nonanoyl chloride and benzophenone oxime according to method A to give **8** (91%) after recrystallisation (pentane), mp 39.6–40.4 °C. δ_H 0.91 (3H, t, $J = 7$), 1.27 (10H, m), 1.59 (2H, m), 2.34 (2H, t, $J = 7$), 7.2–7.6 (10H, m).

***O*-(Trimethylacetyl)benzohydroximoyl chloride 26a.** To a stirred mixture of benzohydroximoyl chloride (10 mmol) and triethylamine (10 mmol) in DCM (50 cm^3) at 0 °C was added the acid chloride (10 mmol) in DCM (10 cm^3) dropwise. The mixture was stirred for 20 min, then 2 M HCl was added (50 cm^3). The organic layer was washed with saturated aqueous sodium bicarbonate (3 × 50 cm^3) and brine (50 cm^3), then dried ($MgSO_4$), and concentrated to give a yellow oil which was purified by bulb-to-bulb distillation (95–100 °C at 0.2 mmHg) to give *O*-(trimethylacetyl)benzohydroximoyl chloride as a colourless liquid (0.88 g; 37%). δ_H 1.38 (9H, s, *t*-Bu), 7.40–7.52 (3H, m, ArH), 7.97–8.00 (2H, d, $J = 7.7$ Hz, ArH). δ_C 27.2, 38.9, 112.6, 128.5, 128.8, 132.2, 174.5. No peak corresponding to the quaternary carbon (Found: M^+, 239.0706. $C_{12}H_{14}{}^{35}ClNO_2$ requires *M*, 239.0708).

***O*-(Valeryl)benzohydroximoyl chloride 26b.** Treatment of benzohydroximoyl chloride with valeryl chloride as described for *O*-(trimethylacetyl)benzohydroximoyl chloride (5 mmol scale) gave an oil which was purified by bulb-to-bulb distillation (100 °C at 0.04 mmHg) to give *O*-(valeryl)benzohydroximoyl chloride as an oil (0.50 g; 42%) which solidified at approximately 10 °C. δ_H 0.97 (3H, t, $J = 7.3$ Hz, -CH_3), 1.42 (2H, m, CH_2CH_3), 1.74 (2H, m, $CH_2CH_2CH_3$), 2.56 (2H, t, $J = 7.4$ Hz, $COCH_2$), 7.4–7.5 (3H, m, ArH), 7.9–8.05 (2H, m, ArH). δ_C 13.6, 22.7, 26.8, 32.3, 128.4, 128.7, 132.2, 131.6, 147.1, 170.1 (Found: M^+, 239.0709. $C_{12}H_{14}{}^{35}ClNO_2$ requires *M*, 239.0708).

***O*-Phenylacetylbenzohydroximoyl chloride 26c.** Treatment of benzohydroximoyl chloride with phenylacetyl chloride as described for *O*-(trimethylacetyl)benzohydroximoyl chloride (5 mmol scale) gave an oil which was purified by bulb-to-bulb distillation (140 °C at 0.04 mmHg) to give *O*-phenylacetylbenzohydroximoyl chloride as an oil (0.68 g; 50%). δ_H 3.87 (2H, s, CH_2), 7.30–7.51 (8H, m, ArH), 7.9–8.0 (2H, m, ArH). δ_C 39.80, 127.69, 128.45, 128.83, 128.96, 129.63, 131.52, 132.33, 132.93, 147.92, 167.83 (Found: M^+, 273.0548. $C_{15}H_{12}{}^{35}ClNO_2$ requires *M*, 273.0552).

Photochemical reaction of *O*-trimethylacetyl benzaldoxime 3a with cyclohex-2-enone

A de-aerated solution of *O*-trimethylacetyl benzaldoxime **3a** (124 mg; 0.61 mmol) and cyclohex-2-enone (124 mg; 1.29 mmol) in DTBP (400 μl) was photolysed for 3 h using a 125 W medium pressure Hg lamp, and the product mixture analysed by GC–MS. Peak no. 101, 1,1-dimethylethanol; peak no. 193, cyclohexenone; peak no. 200, trimethylacetic acid; peak no. 214, benzonitrile; peak no. 308, 3-*tert*-butylcyclohexanone, 154 (M^+) (8), 98 (40), 97 (28), 83 (18), 69 (31), 57 (100), 55 (44), 41 (92), 29 (34), 27 (26); peak nos. 500 and 535, cyclohexenone cycloadducts.

Photochemical reaction of *O*-cyclohexylcarbonyl benzaldoxime 3b with cyclohex-2-enone

A degassed solution of *O*-cyclohexylcarbonyl benzaldoxime **3b** (131 mg; 0.57 mmol), cyclohex-2-enone (230 mg; 2.40 mmol) and DTBP (20 μl) in cyclohexane (500 μl) was photolysed for 6 h using a 125 W medium pressure Hg lamp, and the product mixture analysed by GC–MS. Peak no. 101, 1,1-dimethylethanol; peak no. 193, cyclohexenone; peak no. 211, benzaldehyde; peak no. 214, benzonitrile; peak no. 334, cyclohexanecarboxylic acid; peak no. 445, 3-cyclohexylcyclohexanone, 180 (M^+) (2), 97 (100), 83 (20), 69 (22), 67 (21), 55 (78), 41 (83), 39 (31); peak nos. 504 and 517, cyclohexenone cycloadducts.

Photochemical reactions of *O*-[(cyclohexenyloxy)propionyl] arylaldoximes 3d–7d in DTBP

De-aerated solutions of the *O*-[(cyclohexenyloxy)propionyl] arylaldoximes (~0.065 mmol) in DTBP (150 μl) [or in DTBP (150 μl) and benzene (100 μl) for **5d** and **6d** due to lack of solubility in DTBP] were photolysed for 24 h using a medium pressure 125 W Hg lamp. The mixtures were analysed using GC–MS which showed 1,1-dimethylethanol, the corresponding aromatic aldehyde, the corresponding aromatic nitrile together with several unidentified peaks.

General procedure for photochemical reactions of oxime ethers

A degassed solution of oxime ether (and ~1 equivalent of sensitiser if desired) in the selected solvent (~0.13 M) was photolysed for 3 h in a quartz tube (4 or 10 mm od) using a medium pressure 400 W Hg lamp. A known amount of DCM, 1,4-dioxane or toluene was added, and the reaction yield determined by comparison of the NMR integral trace of a known peak in the product. Reactions were sometimes also analysed by GC–MS.

Reaction of *O*-[(cyclohexenyloxy)propionyl] 2,4-dimethoxybenzaldoxime 4d in 1,2,4-trimethylbenzene. A degassed solution of *O*-[(cyclohexenyloxy)propionyl] 2,4-dimethoxybenzaldoxime (0.0076 g; 0.028 mmol) in 1,2,4-trimethylbenzene (300 μl) was photolysed for 3 h at ~50 °C using a medium pressure 400 W Hg lamp. The product mixture was analysed using GC–MS. Peak no. 94, methylenecyclopentane, *m*/*z* (relative intensity) 82 (M^+) (28), 81 (13), 67 (100), 54 (29), 41 (28), 39 (39), 28 (17), 27 (20).

2-Oxabicyclo[4.3.0]nonane 32.[26] A degassed solution of *O*-[(cyclohexenyloxy)propionyl] 2,4,6-trimethoxybenzaldoxime **5d** (0.25 g; 0.69 mmol) and MAP (0.12 g; 0.80 mmol) in DCM (6 cm^3) was illuminated for 3 h at ~50 °C using a medium pressure 400 W Hg lamp. The mixture was concentrated at room temperature, and the residue repeatedly washed with ether. The solution was again concentrated at room temperature and purified using a microdistillation apparatus to give 2-oxabicyclo[4.3.0]nonane (0.01 g; 12%) as a colourless oil. δ_H 1.15–1.27 (2H, m, CH_2), 1.39–1.68 (6H, m, $3CH_2$), 1.83–2.04 (3H, m, CH_2, CH), 3.75–3.87 (2H, m, OCH_2), 3.97 (1H, q, J = 7.9 Hz).

Acknowledgements

We thank the EPSRC (grant GR/L49185) for financial support of this research and NATO for a travel grant.

References

1 M. Hasebe, K. Kogawa and T. Tsuchiya, *Tetrahedron Lett.*, 1984, **25**, 3887; M. Hasebe and T. Tsuchiya, *Tetrahedron Lett.*, 1986, **27**, 3239.
2 M. Hasebe and T. Tsuchiya, *Tetrahedron Lett.*, 1987, **28**, 6207; M. Hasebe and T. Tsuchiya, *Tetrahedron Lett.*, 1988, **29**, 6287.
3 J. Boivin, A.-M. Schiano and S. Z. Zard, *Tetrahedron Lett.*, 1994, **35**, 249.
4 J. Boivin, A.-C. Callier-Dublanchet, B. Quiclet-Sire, A.-M. Schiano and S. Z. Zard, *Tetrahedron*, 1995, **51**, 6517.
5 J. Boivin, A.-M. Schiano and S. Z. Zard, *Tetrahedron Lett.*, 1992, **33**, 7849.
6 S. Z. Zard, *Synlett*, 1996, 1148.
7 M. Depature, D. Siri, J. Grimaldi, J. Hatem and R. Faure, *Tetrahedron Lett.*, 1999, **40**, 4547.
8 A. J. McCarroll and J. C. Walton, *Chem. Commun.*, 2000, 351.
9 B. S. Furniss, A. J. Hannaford, P. W. G. Smith and A. R. Tatchell, *Vogel's Textbook of Organic Chemistry*, *5th Edition*, Longman, Harlow, 1989.
10 E. V. Aroskar, P. J. N. Brown, R. G. Plevey and R. Stephens, *J. Chem. Soc. C*, 1968, 1569.
11 P. G. Pietta, P. Cavallo and G. R. Marshall, *J. Org. Chem.*, 1971, **36**, 3966.
12 J. Herzig and F. Wenzel, *Monatsh. Chem.*, 1903, **24**, 868.
13 M. Benger and O. L. Brady, *J. Chem. Soc.*, 1950, 1221.
14 P. L. Anelli, C. Banfi, F. Montanari and S. Quici, *J. Org. Chem.*, 1989, **54**, 2970.
15 A. E. J. de Nooy, A. C. Besemer and H. van Bekkum, *Synthesis*, 1996, 1153.
16 A. J. Mancuso and D. Swern, *Synthesis*, 1981, 165.
17 K. S. Webb and S. J. Ruszkay, *Tetrahedron*, 1998, **54**, 401.
18 H. A. Bruson, *Org. React. (N. Y.)*, 1949, **5**, 79.
19 J. H. McGregor and C. Pugh, *J. Chem. Soc.*, 1945, 535.
20 M. Huhtasaari, H. J. Schäfer and L. Becking, *Angew. Chem.*, *Int. Ed. Engl.*, 1984, **23**, 980.
21 H. L. Vaughn and M. D. Robbins, *J. Org. Chem.*, 1975, **40**, 1187.
22 I. Pejković-Tadić, M. Hranisavljević-Jakovljević, S. Nesić, C. Pascual and W. Simon, *Helv. Chim. Acta*, 1965, **48**, 1157.
23 R. F. Hudson and K. A. F. Record, *J. Chem. Soc.*, *Chem. Commun.*, 1976, 539.
24 D. Griller, K. U. Ingold and J. C. Scaiano, *J. Magn. Reson.*, 1980, **38**, 169.
25 L. Grossi and G. Placucci, *J. Chem. Soc.*, *Chem. Commun.*, 1985, 943.
26 A. J. McCarroll and J. C. Walton, *J. Chem. Soc.*, *Perkin Trans. 2*, 2000, 1868.
27 (*a*) G. T. Binmore, J. C. Walton, W. Adcock, C. I. Clark and A. R. Krstic, *Magn. Reson. Chem.*, 1995, **33**, S53; (*b*) A. Mangini, P. Spagnolo, D. Tassi, M. Tiecco and P. Zanirato, *Tetrahedron*, 1972, **28**, 3485; (*c*) L. Testaferri, M. Tiecco, P. Spagnolo, P. Zanirato and G. Martelli, *J. Chem. Soc.*, *Perkin Trans. 2*, 1976, 662; (*d*) D. Griller, P. R. Marriott, D. C. Nonhebel, M. J. Perkins and P. C. Wong, *J. Am. Chem. Soc.*, 1981, **103**, 7761.
28 R. A. Kaba and K. U. Ingold, *J. Am. Chem. Soc.*, 1976, **98**, 7375.
29 A. R. Forrester, M. Gill, J. S. Sadd and R. H. Thomson, *J. Chem. Soc.*, *Perkin Trans. 1*, 1979, 612.
30 K.-C. Liu, B. R. Shelton and R. K. Howe, *J. Org. Chem.*, 1980, **45**, 3916.
31 W. C. Danen and C. T. West, *J. Am. Chem. Soc.*, 1973, **95**, 6872.
32 A. G. Davies, J.-Y. Nedelec and R. Sutcliffe, *J. Chem. Soc.*, *Perkin Trans. 2*, 1983, 209.
33 P. M. Blum and B. P. Roberts, *J. Chem. Soc.*, *Perkin Trans. 2*, 1978, 1313.
34 A. Alberti, G. Barbaro, A. Battaglia, A. Dondoni and G. F. Pedulli, *J. Org. Chem.*, 1980, **45**, 4223.
35 N. H. Anderson, M. McMillan and R. O. C. Norman, *J. Chem. Soc. B*, 1970, 1075.
36 A. H. M. Kayen, Th. A. B. M. Bolsman and Th. J. de Boer, *Recl. Trav. Chim. Pays-Bas*, 1976, **95**, 14.

37 J. Stradins, L. M. Baider, L. Baumane, R. Gavars and V. Glezer, *Elektrokhimiya*, 1977, **13**, 759; A. Berndt, in *Landolt-Börnstein*, *Magnetic Properties of Free Radicals*, vol. 9d1, ed. H. F. Fischer and K.-H. Hellwege, Springer-Verlag, New York, 1980, p. 545.
38 A. R. Forrester, M. Gill, C. J. Meyer, J. S. Sadd and R. H. Thomson, *J. Chem. Soc.*, *Perkin Trans. 1*, 1979, 606.
39 P. H. Ferber, G. E. Gream and T. I. Stoneman, *Aust. J. Chem.*, 1985, **38**, 699.
40 B. R. Cho, N. S. Cho and S. K. Lee, *J. Org. Chem.*, 1997, **62**, 2230; B. R. Cho, W. J. Jang, J. T. Je and R. A. Bartsch, *J. Org. Chem.*, 1993, **58**, 3901.
41 P. T. Gallagher, J. C. A. Hunt, A. P. Lightfoot and C. J. Moody, *J. Chem. Soc.*, *Perkin Trans. 1*, 1997, 2633.