Photolytic and radical induced decompositions of *O*-alkyl aldoxime ethers

Andrew J. McCarroll and John C. Walton *

University of St. Andrews, School of Chemistry, St. Andrews, Fife, UK KY16 9ST

Received (in Cambridge, UK) 25th April 2000, Accepted 1st June 2000
Published on the Web 14th August 2000

Direct photolytic and radical induced homolyses of *O*-alkyl arylaldoxime ethers (ArCH=NOR) were studied by EPR spectroscopy and by end product analyses. Initiating radicals ($X^{\bullet}$), including *t*-$BuO^{\bullet}$, *t*-$BuS^{\bullet}$, alkyl and $Me_3Sn^{\bullet}$, added rapidly to the C=N double bond to give adduct oxyaminyl radicals ($ArCHXN^{\bullet}OR$) that could be observed and characterised by EPR spectroscopy. For *O*-alkyl arylaldoxime ethers containing H-atoms attached to the carbon adjacent to the ether oxygen (OR = $OCHR^1{}_2$), *t*-$BuO^{\bullet}$ radicals also abstracted this hydrogen to yield oxyalkyl radicals that underwent rapid β-scission to afford iminyl radicals ($ArCHN^{\bullet}$) and an aldehyde or ketone ($R^1{}_2CO$). As judged by the relative importance of ROH and ArCN amongst the products, abstraction of the iminyl hydrogen atom also took place to yield oximidoyl radicals ($ArC^{\bullet}$=NOR), although this could not be confirmed by EPR spectroscopic observation of these radicals. Thus, homolysis induced by *t*-$BuO^{\bullet}$ radicals took place comparatively unselectively. Addition of the *t*-$BuO^{\bullet}$ radical to the C=N double bond of oxime ethers was very fast, the rate constant being comparable to that for addition of the same radical to nitrones. Direct and photosensitised UV photolysis of *O*-alkyl arylaldoxime ethers gave alkoxyl and aryliminyl radicals in very low yields. Although traces of 2-methyltetrahydrofuran were detected from cyclisation of the pent-4-enyloxyl radical generated by direct photolysis of *O*-pent-4-enyl benzaldoxime, yields were too low for preparative purposes.

Introduction

We showed recently that aldoxime esters [ArCH=NOC(O)R] could function as useful precursors for iminyl and alkyl radicals when photolysed in the presence of a photosensitiser.[1] It seemed possible that oxime ethers ArCH=N–OR might serve, by means of a similar N–O bond cleavage, as sources of alkoxyl and iminyl radicals. Inter- and intra-molecular additions to oxime ethers are well established for a variety of carbon-centred radicals,[2–6] and use of a Lewis acid was shown to enhance yields.[7] Kinetic data, obtained for several 1,5- and 1,6-*exo*-cyclisations of C-centred radicals onto oxime ethers[6] showed that these additions are exceptionally fast. Recently, Clive and Subedi described an elegant tin hydride mediated cyclisation onto a triphenylmethyl oxime ether, in which the triphenylmethyl radical was expelled, regenerating the oxime functionality.[8] Although there have been no examples of oximyl H-abstractions taking place to yield imidoyl radicals, this might be the result of use of carbon-centred radicals which are electronically unsuitable for this hydrogen abstraction. However, imidoyl radicals have been generated by Nanni *et al.* both by addition to isonitriles, and by hydrogen abstraction by alkoxyl radicals, and put to use in various annulations.[9]

Our objective was to investigate the mechanisms of homolytic reactions of oxime ethers on direct and sensitised photolysis, and in induced reactions with a range of carbon- and hetero-atom centred radicals. EPR Spectroscopy was used to characterise intermediates in the reactions, complemented by end product analyses. A good selection of aryl and alkyl groups within the oxime ether was chosen to compare the effects of substituents with different electron demands.

Results and discussion

Preparation of aldoxime ethers

The oximes chosen for investigation (**1**) were prepared using standard methods from the corresponding aldehyde and hydroxylamine hydrochloride. Most *O*-alkyl benzaldoximes **3** and *O*-alkyl nitrobenzaldoximes **4** were prepared from the oxime and an alkyl bromide in the presence of caesium carbonate in DMF (Method A).[10] Pentafluorobenzaldoxime, 2,4-dimethoxybenzaldoxime and 2,4,6-trimethoxybenzaldoxime ethers could not be prepared using this method, so an alternative route was employed, building on the work of Moody *et al.*, who had shown that *N*-alkoxyphthalimides (prepared from *N*-hydroxyphthalimide and an alcohol under Mitsonobu conditions) could be converted to the corresponding oxime ethers with hydrazine hydrate and benzaldehyde (Scheme 1; Method B).[11] Attempts to make *tert*-butoxyphthalimide failed using Mitsonobu conditions,[12] but an alternative synthesis using *tert*-butyl acetate was carried out successfully.[13] Phthalimide derivatives **2** were converted, as indicated above, to oxime ethers **5**–**7** in good yields (61–70%), except for the *tert*-butyl derivatives for which yields were variable (27–79%).

The oximes, and their ether derivatives, are believed to be the *syn* isomers. The synthesis of benzaldoxime **1** (Ar = Ph) was specific to the *syn* isomer[14] but the other reported syntheses did not indicate which isomers were formed. Pejković-Tadić *et al.* reported that the oximyl hydrogen chemical shifts of various substituted benzaldoximes were dramatically different for the *syn* and *anti* isomers,[15] with all *syn* isomers having protons with $\delta_H > 8$, while the *anti* isomers had $\delta_H < 7.5$ ppm. This distinction enabled us to assign the configurations of **3**–**7** as *syn* with confidence.

EPR Spectroscopic investigation of radical generation from oxime ethers

No radicals were observed when samples of benzaldoxime ethers **3b**, **3c**, 2,4-dimethoxybenzaldoxime ether **6c**, or 2,4,6-trimethoxybenzaldoxime ether **7d**, in *tert*-butylbenzene solvent, were photolysed in the EPR cavity. Similarly, photolyses of a selection of oxime ethers (**3b**, **6c** and **7b**), in the presence of 1 equivalent of *p*-methoxyacetophenone as sensitiser, gave no signals. The only circumstance in which spectra were obtained involved prolonged photolysis (>30 min) of *O*-*tert*-butyl benz-

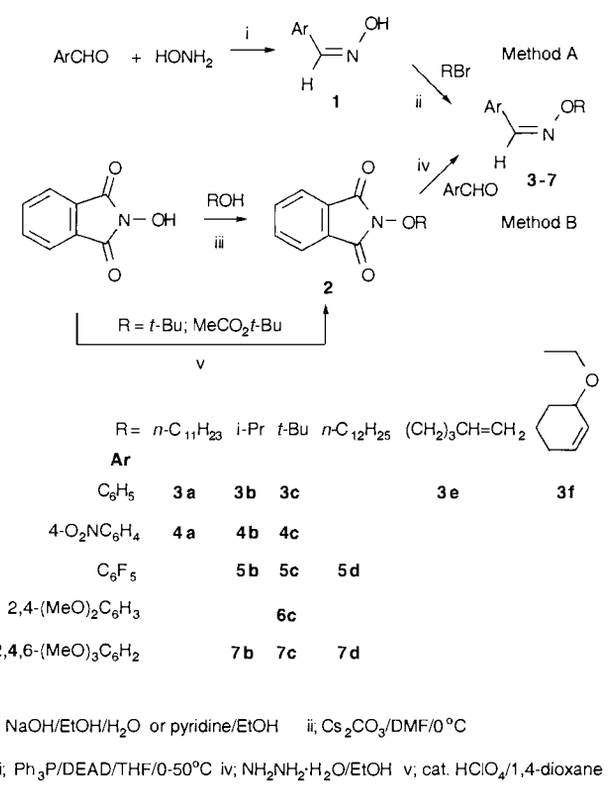
 DOI: 10.1039/b003273p

Table 1 EPR parameters for alkoxyaminyl radicals of type **11** obtained by addition of various radicals to oxime ethers[a]

$$ArCH{=}NOR + X^{\bullet} \longrightarrow ArCH(X){-}N^{\bullet}OR$$

Ar[b]	R[b]	X	*T*/K	*g*-factor	*a*(N)	$a(H_\beta)$	*a*(other)
Ph	C_{11}	*t*-BuO	250	2.0048	13.8	19.3	2.4(2H)
			310		13.8	18.6	2.2(2H), 2.2(1H)
Ph	i-Pr	*t*-BuO	270	2.0049	13.8	19.9	1.6(2H), 2.3(1H)
			340		14.1	16.6	1.9(1H)
Ph	*t*-Bu	*t*-BuO	310		14.4	16.5	
C_6F_5	i-Pr	*t*-BuO	320		13.9	22.5	2.0(1H), 2.0(2F)
C_6F_5	*t*-Bu	*t*-BuO	320		14.6	22.3	3.7(1F + 1F)
C_6F_5	C_{12}	*t*-BuO	320		14.1	22.2	2.3(2F)
DMOP	*t*-Bu	*t*-BuO	320		14.5	16.1	
TMOP	*t*-Bu	*t*-BuO	290		14.3	14.3	
Ph	i-Pr	*t*-BuS	300		14.5	12.4	1.9(1H)
C_6F_5	*t*-Bu	*t*-BuS	320		14.4	21.1	3.6(1F + 1F)
DMOP	*t*-Bu	*t*-BuS	320		14.7	12.1	
Ph	*t*-Bu	Me	300		14.3	16.6	
C_6F_5	*t*-Bu	Me	315		14.3	20.7	2.0(2F)
DMOP	*t*-Bu	Me	320		14.3	16.1	
Ph	*t*-Bu	Et	260	2.0046	14.4	14.4	
C_6F_5	*t*-Bu	Et	270	2.0048	14.1	21.4	3.6(1F + 1F)
			320		14.2	20.7	2.0(2F)
Ph	i-Pr	Me_3Sn	320		14.8	13.6	2.2(1H)
C_6F_5	*t*-Bu	Me_3Sn	320		14.5	21.3	3.7(1F + 1F)
DMOP	*t*-Bu	Me_3Sn	320		14.6	12.2	

[a] Hfs in G. [b] C_{11} = undecyl, C_{12} = dodecyl, DMOP = 2,4-$(MeO)_2C_6H_3$, TMOP = 2,4,6-$(MeO)_3C_6H_2$.



Scheme 1

aldoxime **3c** which resulted in a mixture of radicals, including a persistent radical [*a*(N) = 14.0 G, *a*(H) = 12.4 G at 320 K] which was probably a dialkylaminoxyl. Considering the length of time required for development of these signals it is likely that this, and the other unidentified species, are derived from secondary oxidation processes and are not relevant to our study. In contrast to oxime esters, therefore, direct or photosensitised homolytic cleavage of the N–O bond of oxime ethers did not occur easily.

tert-Butoxyl radicals readily abstract hydrogen from aldehydes and the resulting acyl radicals have been observed by EPR spectroscopy.[16] The imidoyl radical PhC$^{\bullet}$=NBu-*t* was previously generated by hydrogen abstraction with *t*-BuO$^{\bullet}$ radicals from the corresponding aldimine and observed as a singlet by EPR spectroscopy.[17] The possibility that analogous oximidoyl radicals **8** might be spectroscopically observable on hydrogen abstraction by this electrophilic radical, from oxime ethers **3**–**7**, was therefore checked by photolyses in neat di-*tert*-butyl peroxide (DTBP), and of solutions in *tert*-butylbenzene. No spectra were obtained from *O*-alkyl *p*-nitrobenzaldoximes (**4a**–**c**) under these conditions. However, clear EPR spectra were obtained from most of the other oxime ethers. Each *O*-*tert*-butyl arylaldoxime gave a single spectrum showing hyperfine splitting (hfs) from one N-atom of *ca.* 14 G† and one H-atom of 12–23 G (Table 1). These hfs, and the measured *g*-factors of *ca.* 2.0048, are similar to the EPR parameters of alkoxyaminyl radicals such as i-PrN$^{\bullet}$OCH$_3$ (*g* = 2.0046, *a*(N) = 13.96, *a*(1H) = 18.8, *a*(3H) = 2.56 G at 210 K in toluene),[18] and to the parameters reported for an alkoxyaminyl radical adduct obtained from addition to the *tert*-butoxymethyl oxime ether of 2-phenylbenzaldehyde [ArCHXN$^{\bullet}$OCH$_2$OBu-*t* (X unknown) *g* = 2.0049, *a*(N) = 14.35, *a*(1H) = 20.0, *a*(2H) = 2.62 G at 348 K].[19] We therefore attribute the spectra to adduct aminyl radicals **11** rather than to oximidoyl radicals. No imidoyl spectra were apparent, even in photolyses carried out at a temperature as low as 160 K in cyclopropane solution.

The aminyl spectra were generally stronger at higher temperatures (≥300 K) and persisted for many minutes in the dark, especially for the *O*-*tert*-butyl derivatives. Weak spectra of an aminoxyl, and of one unidentified radical, accompanied that of radical **11** in the case of **3c**, especially after prolonged photolysis.

Photolyses of *O*-undecyl **3a** and *O*-isopropyl **3b** benzaldoximes in neat DTBP displayed the EPR spectra of the corresponding oxyaminyls (**11**), each accompanied by iminyl radical **13** (Ar = Ph) with a very large and characteristic hfs from a single H-atom [*a*(N) = 9.68, *a*(1H) = 79.66 G at 250 K]. The spectrum of the radicals obtained from **3a** is shown in Fig. 1.

While it is possible that the formation of the iminyl radical could have been due to direct homolysis of the N–O bond, it is much more likely that this was caused by abstraction of the activated hydrogen, adjacent to oxygen, in the alkyl chains of **3a**,**b** followed by β-scission of the resulting imino-oxyalkyl radical **12** (Scheme 2). There is a precedent for this process in that

† 10 G = 1 mT.

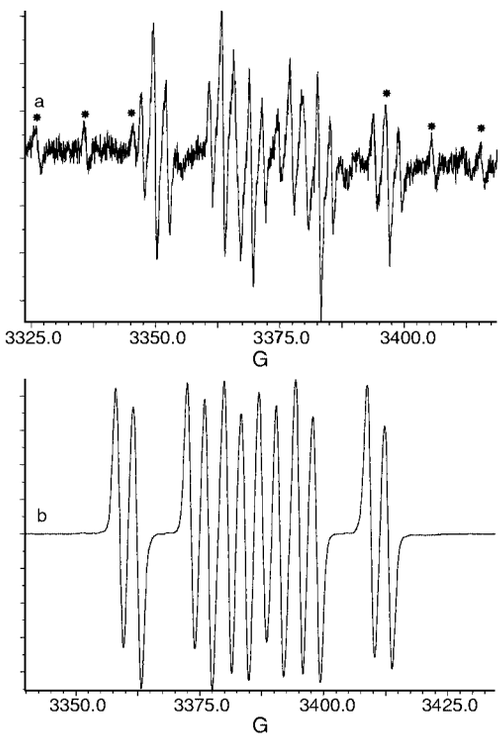
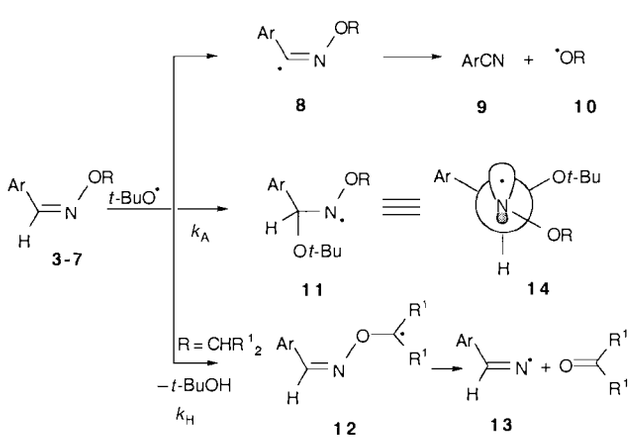


Fig. 1 (a) Upper spectrum: 9.4 GHz EPR spectra obtained on photolysis of *O*-undecyl benzaldoxime ether **3a** in DTBP at 250 K. Central features are due to the adduct oxyaminyl radical **11** (R = undecyl), outer lines (starred) are due to iminyl radical **13** (Ar = Ph). (b) Lower spectrum: 9.4 GHz EPR spectrum obtained on photolysis of *O*-*tert*-butyl pentafluorobenzaldoxime ether **5c** and di-*tert*-butyl peroxyoxalate in *tert*-butylbenzene at 350 K.

analogous β-scissions have been reported for imino-oxymethyl radicals generated by other routes.[20] Furthermore, the relative intensity of the iminyl radical signal obtained from isopropyl ether **3b** was much greater than that obtained from undecyl ether **3a**. This is consistent with easier abstraction by *t*-BuO$^{\bullet}$ radicals of the secondary H-atom in **3b** than the primary H-atoms in **3a**. The absence of the iminyl radical in the reaction of *O*-*tert*-butyl benzaldoxime **3c** provided additional evidence for this mechanism, because the *tert*-butyl group contains no readily abstractable hydrogens. In addition, product analyses with **3a** demonstrated the formation of undecanal, the co-product expected from the β-scission (see below). The spectrum of iminyl radical **13** (Ar = 2,4,6-$(MeO)_3C_6H_2$) was observed on photolysis of *O*-dodecyl 2,4,6-trimethoxybenzaldoxime **7d** in the presence of DTBP in the EPR cavity. Formation of this radical can be attributed to the same H-abstraction/β-scission process (Scheme 2). EPR Spectroscopic investigation of the



Scheme 2

reactions of pentafluorobenzaldoxime ethers **5b–d** with DTBP under the same conditions revealed strong spectra of analogous alkoxyaminyl radicals **11** (Fig. 1). In this instance, no iminyl radicals were detected from the primary **5d** or secondary **5b** precursors at any time. It seems probable that addition to afford aminyls **11** is faster for these oxime ethers and the H-abstraction process from the alkyl chains does not compete effectively.

tert-Butoxyl radicals are known for being efficient at H-abstraction, rather than at addition to carbon–carbon double bonds. The oxyaminyl radicals **11** displayed no resolved long range hfs from the original trapped radical (X) and therefore their identity could not be unequivocally confirmed from the EPR spectra. Although this lack of long range hfs was as expected for *t*-BuO$^{\bullet}$, as the O-atom has no nuclear spin, the possibility that in fact some other radical was being trapped needed to be addressed. Identical spectra were obtained in neat DTBP, and in *tert*-butylbenzene solvent, so the trapped radical was not derived from the solvent. When an alternative source of *t*-BuO$^{\bullet}$ radicals, namely di-*tert*-butyl peroxyoxalate, was employed in place of DTBP, identical spectra of the oxyaminyl adducts were obtained. It is most likely, therefore, that the adding species is the *t*-BuO$^{\bullet}$ radical. Addition by C-centred radicals to oxime ethers was known to be faster than to alkenes and our results suggest that addition of *t*-BuO$^{\bullet}$ radicals to oxime ethers is also enhanced.

Radical addition to oxime ethers was further investigated by generation of a range of radicals, centred on different elements, in the presence of the oxime ethers **3**–**7**. *t*-BuS$^{\bullet}$ radicals, generated by photolysis of *t*-BuSSBu-*t*, $Me_3Sn^{\bullet}$ radicals generated from hexamethylditin and Me$^{\bullet}$ radicals generated from diacetyl peroxide, all gave rise to good EPR spectra of the corresponding oxyaminyl adducts ArCH(X)N$^{\bullet}$OR (Table 1). The EPR hfs of all these aminyls were broadly similar but sufficiently different in each case to distinguish them, even though no long range hfs from the trapped species were resolved. Ethyl radicals were generated from photolysis of DTBP in the presence of Et_3B. Reaction in the presence of **3c** showed the spectrum of the ethyl radical at 210 K, but this was gradually replaced, as the temperature was increased, by the spectrum of the aminyl adduct PhCH(Et)N$^{\bullet}$OBu-*t* (Table 1). A similar sequence was observed for the pentafluoro analogue **5c**. No iminyl radicals were detected in the reactions of *t*-BuS$^{\bullet}$, or $Me_3Sn^{\bullet}$ with the isopropyl oxime ether **3b**, as would be expected for these poor hydrogen abstractor radicals.

The values of the EPR hfs of oxyaminyl radicals **11** are about normal for aminyls, as indicated above. The hfs of the β-hydrogens varied in the range 12–23 G depending on the nature of the aryl group and the substituent X. For all the adducts the magnitude of $a(H_\beta)$ decreased as the temperature increased; see Table 1 for some representative examples. It is probable, therefore, that the preferred, low temperature, conformation about the N$^{\bullet}$–C_β bond has the SOMO and the C–H_β eclipsing one another, *i.e.* as shown in structure **14**. In this conformation steric strain is minimised because the bulky aryl group and the alkoxy group avoid one another in an *anti* arrangement. Long range hfs from hydrogens on the *O*-Pr-i and *O*-alkyl-*n* chains could be observed and showed little variation from radical to radical. The long range hfs from aryl H- and F-atoms showed significant variations with temperature. In particular, the aminyl radical $C_6F_5CH(Et)N^{\bullet}OBu$-*t* displayed an apparent doublet long range splitting of 3.6 G at 270 K (the lowest temperature at which it could be observed) but on warming this developed into a triplet by the appearance and growth of a central line. It is likely that the doublet was actually the outer pair of lines from a double doublet, due to two non-equivalent F-atoms; the central pair being too broad to observe at 270 K. As the temperature increased, the rates of internal rotations about the Ar–C_β and/or C_β–N$^{\bullet}$ bonds increased until the two F-atoms were equivalent on the EPR timescale at temperatures above *ca.* 320 K, thus leading to the observed triplet.

Table 2 Relative rate constants for *t*-BuO$^{\bullet}$ radical addition and H-abstraction from oxime ethers **3a** and **3b**

	T/K	180[a]	190[a]	251	251	272	277	292	302	312	323
3a:	k_A/k_H	4.4	3.8	18.8	19.0			26.1	46.4	46.2	
3b:	k_A/k_H			0.98		2.9	3.5		10.9		14.9

[a] In cyclopropane solvent; other results in neat di-*tert*-butyl peroxide.

It follows that the apparent doublets of 3.6–3.7 G recorded for the other C_6F_5 aminyls (Table 1) were probably also parts of double doublets. The central N-atoms of oxyaminyls **11**, particularly those with OR = OBu-*t*, are surrounded by bulky groups, and this steric shielding accounts for their observed persistence.

We attempted to cross-check for oximidoyl radicals (**8**) by chlorine atom abstraction from *O*-alkyl benzohydroximoyl chlorides (PhCCl=NOR) by trimethyltin radicals. *O*-Alkyl benzohydroximoyl chlorides were prepared from potassium benzohydroxamate[21] according to the method of Johnson *et al.*[22,23] Treatment of *O*-*n*-propyl and *O*-isopropyl benzohydroxamates with phosphorus pentachloride gave the corresponding *O*-alkyl benzohydroximoyl chlorides, albeit in poor overall yields. Photolyses of solutions of each of these chlorides and hexamethylditin in *tert*-butylbenzene in the EPR cavity gave rise to the same spectrum (a(N) = 14.1, a(3H) = 3.6, a(2H) = 1.2 G at 270 K). This species is obviously not an oximidoyl radical but it remains unidentified.

Relative rates of addition to and H-abstraction from oxime ethers

Imino-oxyalkyl radicals **12** were not observed by EPR spectroscopy for any of the oxime ethers at any temperature. This implies that their β-scission to iminyl radicals is fast, and consequently that their instantaneous concentration is negligible; application of the steady state approximation to the mechanism shown in Scheme 2 leads to the kinetic expression eqn. (1) for

$$[\mathbf{11}]/[\mathbf{13}] = k_A/k_H \qquad (1)$$

addition of *t*-BuO$^{\bullet}$ to the >C=N–OCHR$^1_2$ double bond (k_A) and abstraction of the –OCHR$^1_2$ hydrogen-atom (k_H).

In deriving eqn. (1) it has been assumed that the termination rates of the oxyaminyl radicals **11** and iminyl radicals **13** are fast, at about the diffusion limit, and that the rate constants ($2k_t$) are equal. The ratios of the derived oxyaminyl and iminyl radicals were determined for oxime ethers **3a** and **3b** in neat di-*tert*-butyl peroxide and/or cyclopropane solution, at a series of temperatures, by double integration of appropriate lines in the EPR spectra. Table 2 shows the derived relative rate constants. Linear regression gave good straight lines (Fig. 2) and the following Arrhenius parameters:

3a: $\log(A_A/A_H) = 3.1 \pm 0.5$, $E_A - E_H$/kcal mol$^{-1} = 2.1 \pm 0.3$, $k_A/k_H(300\ K) = 37.6$.

3b: $\log(A_A/A_H) = 5.5 \pm 0.5$, $E_A - E_H$/kcal mol$^{-1} = 6.3 \pm 0.6$, $k_A/k_H(300\ K) = 8.3$.

The rate constants for H-abstraction from structures –OCH$_2$R by *t*-BuO$^{\bullet}$ radicals range from[24] 2 to 8×10^6 dm^3 mol^{-1} s^{-1} depending on the nature of R and of the group attached to oxygen. Combination of these k_H's with the above experimental data implies that k_A is in the range 8 to 30×10^7 dm^3 mol^{-1} s^{-1} at 300 K. This is the same order of magnitude as for *t*-BuO$^{\bullet}$ addition to nitrones (0.5 to 50×10^7 dm^3 mol^{-1} s^{-1})[25] (and for cyclisation of C-centred radicals onto oxime ethers).[2]

Photochemical reactions of oxime ethers

Photolysis of a solution of undecyl oxime ether **3a** in toluene either alone, or in the presence of 4-methoxyacetophenone (PMAP) as photosensitiser, for up to 24 h led to only very low conversions (≤5%). The only products detected by GC/MS

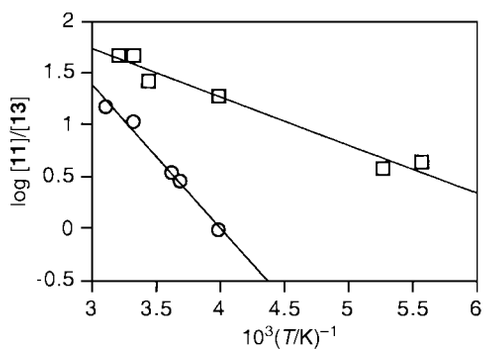
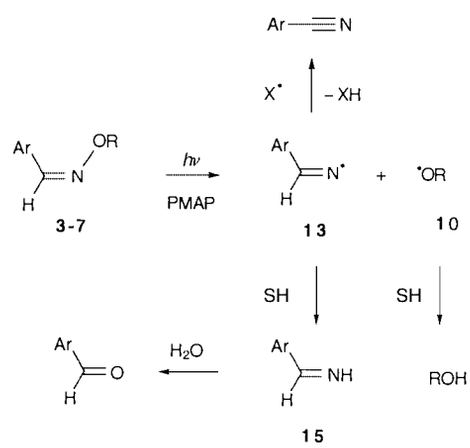


Fig. 2 Arrhenius plots of the relative rate constants for *t*-BuO$^{\bullet}$ radical addition to and H-abstraction from oxime ethers **3a** and **3b**. Upper line (squares) for **3a**, $r^2 = 0.967$. Lower line (circles) for **3b**, $r^2 = 0.986$.

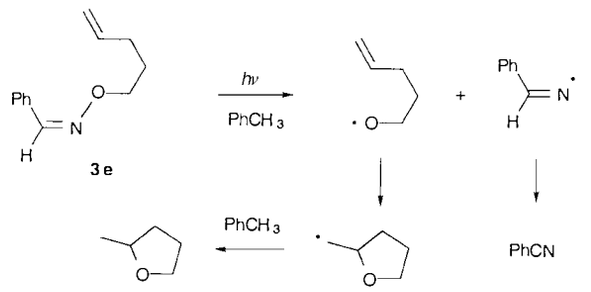
were undecanal, undecanol, benzaldehyde and benzonitrile. The fact that minor quantities of these products were observed in the absence of an initiator indicated that a small amount of direct N–O bond cleavage did occur although the quantum yield was obviously trifling. Evidently, the stationary concentration of iminyl **13** formed in this way was too low for EPR spectroscopic detection. A plausible mechanism for formation of these products is shown in Scheme 3. The iminyl radical **13**



Scheme 3

may lose a hydrogen atom to some radical X$^{\bullet}$ which may be RO$^{\bullet}$, or another iminyl, to produce the benzonitrile or, alternatively, abstract hydrogen from the solvent (SH) to yield aldimine **15** which hydrolyses to benzaldehyde, probably during analysis. The undecanol will be formed by hydrogen abstraction by the alkoxyl radical. The smaller amounts of undecanal could be due to disproportionation of undecanoxyl radicals.

The occurrence of direct photochemical N–O bond scission was confirmed by irradiation of a degassed mixture of *O*-pent-4-enyl benzaldoxime **3e** in toluene for 3 h. GC/MS analysis revealed 2-methyltetrahydrofuran and benzonitrile as the only detectable products; conversion was very low. The 2-methyltetrahydrofuran was formed by cyclisation of the intermediate pent-4-enyloxyl radical (Scheme 4). This indicates that photolysis of the oxime ether does result in direct cleavage of the N–O bond, but only to a very small extent.



Scheme 4

Photolysis of **3a** in neat DTBP at 25 °C for 6 h using a medium pressure Hg lamp also gave low conversion and formation of the same products, accompanied by *tert*-butyl alcohol and minor amounts of longer retention time products which could not be identified with certainty, but were probably derived from adduct radicals **11**. Conversion was not improved by the use of methyl thioglycolate as a potential 'Polarity Reversal' catalyst.[26]

The reactions shown in Scheme 2 will accompany the direct N–O bond scission in the presence of *t*-BuO$^{\bullet}$ radicals. Thermal reactions initiated with benzoyl peroxide and *tert*-butyl peroxyoxalate were also carried out and gave the same products as those obtained under photolytic conditions. *O*-Alkyl arylaldoximes **4a**, **5d**, and **7d** all gave undecyl or dodecyl alcohol, along with the corresponding aldehyde and aryl nitrile, under photolytic conditions in the presence of DTBP, as described for **3a**. Under all circumstances the amount of undecanol (or dodecanol) significantly exceeded the amount of undecanal (or dodecanal) formed. Similarly, the amount of aryl nitrile exceeded that of benzaldehyde. It was not possible to quantify the proportion of direct homolysis (Scheme 3) compared to induced decomposition (Scheme 2), but the analyses suggested that the latter was more important. If this is correct it would be expected that undecanal (or dodecanal) would predominate (see Scheme 2) contrary to our observations, unless the *t*-BuO$^{\bullet}$ radicals also abstracted the iminyl hydrogen to yield oximidoyl radicals **8** which then fragmented to give the aryl nitrile **9** and alkoxyl radical **10** (Scheme 2). This would explain the formation of comparatively large amounts of ROH and **9**.

Conclusions

Direct and photosensitised UV photolysis of *O*-alkyl benzaldoxime ethers was much less efficient than that of oxime esters. Yields were not high enough for EPR spectroscopic detection of the intermediate radicals or for the process to be a preparatively useful route to alkoxyl radicals. Incorporation of electron-releasing or electron-withdrawing substituents into the aromatic ring did not significantly improve this situation. Homolysis of *O*-alkyl arylaldoxime ethers induced by *tert*-butoxyl radicals took place indiscriminately. Initiating radicals, including *t*-BuO$^{\bullet}$, *t*-BuS$^{\bullet}$, alkyl and $Me_3Sn^{\bullet}$ added rapidly to the C=N double bond to give adduct oxyaminyl radicals that could be observed and characterised by EPR spectroscopy. For *O*-alkyl arylaldoxime ethers containing H-atoms attached to the carbon adjacent to the ether oxygen (–OCHR$_2$), *t*-BuO$^{\bullet}$ radicals also abstracted this hydrogen to yield oxyalkyl radicals that underwent rapid β-scission to afford iminyl radicals and an aldehyde. As judged by the relative importance of ROH and ArCN amongst the products, abstraction of the iminyl hydrogen atom also took place to yield oximidoyl radicals, although this could not be confirmed by EPR spectroscopic observation of these radicals. Thus, as is usual for *t*-BuO$^{\bullet}$ radicals, attack at all possible sites took place, with comparatively low selectivity. The most interesting contrast with analogous reactions of alkenes was the fast addition of electrophilic *t*-BuO$^{\bullet}$ radicals to the C=N double bond, the rate constant being comparable to that for addition of the same radical to nitrones.

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 deaerated 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*-alkyl benzohydroximoyl 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. *tert*-Butyl hydroperoxide was purified by distilling in a Dean–Stark apparatus to remove water, and then distilling at water pump pressure. Other organic compounds were used as received. Column chromatography was performed using BDH silica gel (40–63 mm).

syn-Benzaldoxime,[14] *p*-nitrobenzaldoxime,[14] pentafluorobenzaldoxime,[27] 2,4-dimethoxybenzaldoxime,[28] 2,4,6-trimethoxybenzaldoxime,[29] *N*-*tert*-butoxyphthalimide,[13] *N*-isopropoxyphthalimide,[30] potassium benzohydroximate,[21] *O*-isopropyl benzohydroxamate,[22] *O*-*n*-propyl benzohydroxamate,[23] *O*-isopropyl benzohydroximoyl chloride,[22] *O*-*n*-propyl benzohydroximoyl chloride[23] and di-*tert*-butyl peroxyoxalate[31] were prepared as described in the literature.

N-Dodecoxyphthalimide 2d

This was prepared from dodecanol (9.25 mmol) and *N*-hydroxyphthalimide and purified in the same way as *N*-isopropoxyphthalimide,[30] to give *N*-dodecoxyphthalimide (2.11 g; 69%) as white crystals, mp 64–65 °C. δ_H 0.88 (3H, t, J = 6.6 Hz, –CH$_3$), 1.26–1.31 (16H, m, 8-CH$_2$–), 1.45–1.50 (2H, m, –OCH$_2$-CH$_2$CH$_2$–), 1.77–1.82 (2H, m, –OCH$_2$CH$_2$), 4.22 (2H, t, J = 6.7 Hz, –OCH$_2$–), 7.73–7.76 (2H, m, ArH), 7.83–7.87 (2H, m, ArH); δ_C 14.1, 22.7, 25.6, 28.2, 29.4, 29.5, 29.6, 29.7, 32.0, 78.8, 123.7, 129.2, 134.6, 163.9 (Found: C, 72.5; H, 8.8; N, 4.3. Calc. for $C_{20}H_{29}NO_3$: C, 72.5; H, 8.8; N, 4.2%).

Typical syntheses of *O*-alkyl benzaldoximes

Method A: To a stirred mixture of oxime (12 mmol) and alkyl bromide (10 mmol) in DMF (33 cm^3) at 0 °C was added caesium carbonate (3.98 g; 12 mmol). The mixture was stirred overnight. Water (25 cm^3) was added, and the product was extracted with ether (3 × 25 cm^3), then washed extensively with

water, and the organic layer dried ($MgSO_4$) and concentrated. Recrystallisation or column chromatography yielded pure product.

Method B: A suspension of *N*-alkoxyphthalimide (3.31 mmol) in ethanol (5 cm^3) was heated until the solid dissolved. Hydrazine hydrate (180 μl; 3.64 mmol) was added, and the mixture stirred at the elevated temperature for a few minutes, then allowed to cool to room temperature. Arylaldehyde (3.50 mmol) was added, and the mixture stirred overnight. The mixture was filtered, then concentrated. DCM was added (~10 cm^3) and the mixture filtered again. Column chromatography yielded pure product.

O-Undecyl benzaldoxime 3a

Prepared from benzaldoxime and undecyl bromide according to method A to give *O*-undecyl benzaldoxime as a colourless oil (1.41 g; 51%) after column chromatography (PE–EtOAc). δ_H 0.85–0.90 (3H, t, J = 7.1 Hz, $–CH_3$), 1.26–1.38 (16H, m, alkyl H), 1.68–1.73 (2H, m, $–OCH_2CH_2–$), 4.17 (2H, t, J = 6.8 Hz, $–OCH_2–$), 7.35–7.37 (3H, m, ArH), 7.56–7.59 (2H, m, ArH), 8.07 (1H, s, –CH=N–); δ_C 14.1, 22.7, 25.9, 29.1, 29.3, 29.5, 29.6, 31.9, 74.4, 126.9, 128.6, 129.6, 132.8, 148.2; *m*/*z* (%) 274 ($M^+ - 1$) (1), 244 (3), 146 (10), 132 (12), 104 (29), 77 (34), 57 (48), 55 (44), 43 (100), 41 (83) (Found: M^+, 275.2258. $C_{18}H_{29}NO$ requires *M*, 275.2249).

O-Isopropyl benzaldoxime 3b[32]

Prepared from benzaldoxime and isopropyl bromide according to method A to give *O*-isopropyl benzaldoxime as a colourless oil (1.27 g; 78%) after column chromatography (PE–EtOAc). δ_H(200 MHz) 1.27 (6H, d, J = 6.2 Hz, $2CH_3$), 4.17 (1H, septet, J = 6.7 Hz, $CH(CH_3)_2$), 7.35–7.40 (3H, m, ArH), 7.56–7.61 (2H, m, ArH), 8.08 (1H, s, CH=N).

O-*tert*-Butyl benzaldoxime 3c

Prepared from benzaldehyde and *N*-*tert*-butoxyphthalimide according to method B to give *O*-*tert*-butyl benzaldoxime (0.26 g; 44%) as a colourless oil after column chromatography (PE–DCM). δ_H 1.36 (9H, s, *t*-Bu), 7.36 (3H, m, ArH), 7.60 (2H, m, ArH), 8.05 (1H, s, CH=N); δ_C 27.7, 79.3, 127.0, 128.8, 129.5, 133.5, 147.4 (Found: M^+, 177.1148. $C_{11}H_{15}NO$ requires *M*, 177.1153).

O-Pent-4-enyl benzaldoxime 3e

Prepared from benzaldoxime and 5-bromopent-1-ene according to method A to give *O*-pent-4-enyl benzaldoxime as a colourless oil (1.52 g; 80%) after column chromatography (PE–DCM). δ_H 1.77–1.87 (2H, m, $–CH_2CH_2CH_2–$), 2.14–2.21 (2H, m, $–CH_2CH=$), 4.18 (2H, t, J = 6.6 Hz, $–OCH_2–$), 4.97–5.10 (2H, m, $CH_2=CH–$), 5.78–5.92 (1H, m, $CH_2=CH–$), 7.34–7.38 (3H, m, ArH), 7.55–7.60 (2H, m, ArH), 8.07 (1H, s, –CH=N–); δ_C 28.4, 30.0, 73.7, 115.0, 127.1, 128.8, 129.8, 132.6, 148.5 (Found: M^+, 189.1154. $C_{12}H_{15}NO$ requires *M*, 189.1149).

O-2-(Cyclohexen-3-yloxy)ethyl benzaldoxime 3f

Prepared from benzaldoxime and 3-(2-bromoethoxy)cyclohexene according to method A to give *O*-2-(cyclohexen-3-yloxy)ethyl benzaldoxime as a colourless oil (0.65 g; 55%), δ_H 1.66–2.04 (6H, m, alkyl Hs), 3.75–3.87 (2H, m, $–OCH_2$), 3.93 (1H, m, $–OCHR_2$), 4.32 (2H, t, J = 5.1 Hz, OCH_2), 5.77–5.87 (2H, m, HC=CH), 7.37 (3H, t, J = 3.1 Hz, ArH), 8.13 (1H, s, –CH=N–); δ_C 19.3, 25.3, 28.3, 66.5, 73.5, 74.0, 127.3, 128.0, 128.9, 130.0, 131.1, 149.1 (Found: M^+, 245.1423. $C_{15}H_{19}NO_2$ requires *M*, 245.1416).

O-Undecyl *p*-nitrobenzaldoxime 4a

Prepared from *p*-nitrobenzaldoxime and undecyl bromide according to method A to give *O*-undecyl *p*-nitrobenzaldoxime (1.00 g; 62%) as white crystals, mp 41–43 °C after column chromatography (PE–EtOAc). δ_H 0.87 (3H, t, J = 6.7 Hz, $-CH_3$), 1.26 (16H, m, $8 \times CH_2$), 1.73 (2H, m, J = 7.1 Hz, $–OCH_2CH_2–$), 4.21 (2H, t, J = 6.7 Hz, $–OCH_2$) 7.73 (2H, d, J = 8.8 Hz, ArH), 8.12 (1H, s, CH=N), 8.22 (2H, d, J = 8.8 Hz, ArH); δ_C 14.1, 22.7, 25.9, 29.2, 29.4, 29.5, 29.7, 32.0, 75.4, 124.2, 127.6, 139.0, 146.1, 148.5 (Found: M^+, 320.2106. $C_{18}H_{28}N_2O_3$ requires *M*, 320.2100).

O-Isopropyl *p*-nitrobenzaldoxime 4b

Prepared from *p*-nitrobenzaldoxime and isopropyl bromide according to method A to give *O*-isopropyl *p*-nitrobenzaldoxime (0.99 g; 95%) as pale yellow crystals, mp 51.5–53 °C after column chromatography (PE–EtOAc). δ_H 1.32 (6H, d, J = 6.2 Hz, $CH(CH_3)_2$), 4.46–4.54 (1H, septet, J = 6.2 Hz, $CH(CH_3)_2$), 7.76 (2H, d, J = 8.6 Hz, ArH), 8.09 (1H, s, CH=N), 8.22 (2H, d, J = 8.6 Hz, ArH); δ_C 21.1, 123.3, 123.7, 127.1, 131.1, 138.7, 142.4 (Found: C, 57.85; H, 5.48; N, 13.45. Calc. for $C_{10}H_{12}N_2O_3$: C, 57.69; H, 5.81; N, 13.45%).

O-*tert*-Butyl *p*-nitrobenzaldoxime 4c

Prepared from *p*-nitrobenzaldehyde and *N*-*tert*-butoxyphthalimide according to method B to give *O*-*tert*-butyl *p*-nitrobenzaldoxime (0.41 g; 65%) as pale yellow crystals, mp 59–60.5 °C after column chromatography (PE–DCM). δ_H 1.37 (9H, s, $–C(CH_3)_3$), 7.74 (2H, d, J = 8.8 Hz, ArH), 8.09 (1H, s, –CH=N–), 8.22 (2H, d, J = 8.8 Hz, ArH); δ_C 27.5, 80.5, 124.2, 127.5, 131.5, 139.6, 145.3 (Found: C, 59.6; H, 6.4; N, 12.7. Calc. for $C_{11}H_{14}N_2O_3$: C, 59.5; H, 6.4; N, 12.6%).

O-Isopropyl pentafluorobenzaldoxime 5b

Prepared from pentafluorobenzaldehyde and *N*-isopropoxyphthalimide according to method B to give *O*-isopropyl pentafluorobenzaldoxime (0.52 g, 62%) as a colourless oil after column chromatography (DCM). δ_H 1.26 (6H, d, J = 6.0 Hz, $CH(CH_3)_2$), 4.49–4.61 (1H, septet, J = 6.3 Hz, $CH(CH_3)_2$), 8.11 (1H, s, CH=N); δ_C 21.45, 107.97–108.37 (m), 131.28, 135.93–136.20 (m), 136.43, 139.26–139.72 (m), 142.78–143.32 (m), 146.47–146.76 (m) (Found: M^+, 267.0526. $C_{11}H_{10}F_5NO$ requires *M*, 267.0532).

O-*tert*-Butyl pentafluorobenzaldoxime 5c

Prepared from pentafluorobenzaldehyde and *N*-*tert*-butoxyphthalimide according to method B to give *O*-*tert*-butyl pentafluorobenzaldoxime (0.48 g; 54%) as a colourless oil after column chromatography (PE–DCM). δ_H 1.36 (9H, s, *t*-Bu), 8.10 (1H, s, CH); δ_C 27.39, 80.78, 108.34–108.69 (m), 130.73, 135.78, 136.11–136.33 (m), 139.30–139.61 (m), 142.59–143.35 (m, possibly two overlapping multiplets), 146.44–146.69 (Found: M^+, 237.1357. $C_{11}H_{10}F_5NO$ requires *M*, 237.1365).

O-Dodecyl pentafluorobenzaldoxime 5d

Prepared from pentafluorobenzaldehyde and *N*-dodecyloxyphthalimide according to method B (on a 1.65 mmol scale) to give *O*-dodecyl pentafluorobenzaldoxime (0.38 g, 61%) as a colourless oil after column chromatography (DCM). δ_H 0.88 (3H, t, J = 6.7 Hz, $–CH_3$), 1.26–1.54 (18H, m, alkyl Hs), 1.67–1.74 (2H, m, $–OCH_2CH_2–$), 4.20–4.25 (2H, t, J = 6.7 Hz, $–OCH_2–$), 8.13 (1H, s, CH=N); δ_C 14.12, 22.69, 25.79, 29.01, 29.35, 29.39, 29.56, 29.60, 29.65, 31.93, 53,42, 75.48, 131.66, ~136.1, (m), 136.80, 139.48–139.61 (m), 143.02–143.20 (m), 146.6 (m).

O-*tert*-Butyl 2,4-dimethoxybenzaldoxime 6c

Prepared from *tert*-butoxyphthalimide and 2,4-dimethoxybenzaldoxime according to method B to give *O*-*tert*-butyl 2,4-dimethoxybenzaldoxime as a colourless oil (0.31 g; 79%). δ_H

1.36 (9H, s, –C(CH_3)$_3$), 3.81 (6H, s, –OMe), 6.45 (1H, t, J = 2.2 Hz, ArH), 6.75 (2H, d, J = 2.5 Hz, ArH), 7.96 (1H, s, –CH=N–); δ_C 27.5, 55.3, 79.2, 101.6, 104.8, 147.2, 161.0 (Found: M^+, 237.1358. $C_{13}H_{19}NO_3$ requires M, 237.1365).

O-Isopropyl 2,4,6-trimethoxybenzaldoxime 7b

Prepared from *N*-isopropoxyphthalimide and 2,4,6-trimethoxybenzaldehyde according to method B to give *O*-isopropyl 2,4,6-trimethoxybenzaldoxime as a colourless oil (0.59 g; 70%) after column chromatography (DCM). *Z* isomer: δ_H 1.30 (6H, d, J = 6.1 Hz, –CH(CH_3)$_2$), 3.82 (9H, s, (OCH_3)$_3$), 4.42–4.50 (1H, m, –CH(CH_3)$_2$), 6.12 (2H, s, ArH), 8.35 (1H, s, –CH=N–). *E* isomer 1.23 (6H, d, J = 6.3 Hz, –CH(CH_3)$_2$), 3.82 (9H, s, (OCH_3)$_3$), 4.42–4.50 (1H, m, –CH(CH_3)$_2$), 6.11 (2H, s, ArH), 7.34 (1H, s, –CH=N–); δ_C (*Z* only) 21.7, 55.3, 56.0, 74.9, 91.0, 103.3, 143.5, 160.2, 162.3 (Found: M^+, 253.1319. $C_{13}H_{19}NO_4$ requires M, 253.1314).

O-*tert*-Butyl 2,4,6-trimethoxybenzaldoxime 7c

Prepared from *N*-*tert*-butoxyphthalimide and 2,4,6-trimethoxybenzaldehyde according to method B to give *O*-*tert*-butyl 2,4,6-trimethoxybenzaldoxime as white needles, which contained *tert*-butoxyphthalimide impurity that could not be removed by column chromatography or recrystallisation. δ_H 1.36 (9H, s, C(CH_3)$_3$), 3.82 (9H, s, 3OMe), 6.13 (2H, s, ArH), 8.32 (1H, s, CH=N); δ_C 27.4, 55.4, 56.2, 78.2, 91.4, 104.2, 142.7, 160.2, 162.1.

O-Dodecyl 2,4,6-trimethoxybenzaldoxime 7d

Prepared from *N*-dodecyloxyphthalimide and 2,4,6-trimethoxybenzaldehyde (on a 1.65 mmol scale) according to method B to give *O*-dodecyl 2,4,6-trimethoxybenzaldoxime (0.38 g; 61%) as a colourless oil after column chromatography (DCM), which crystallised slowly, mp 32.0–32.5 °C. δ_H 0.87 (3H, t, J = 7.1 Hz, –CH_3), 1.25–1.38 (18H, m, 9 × –CH_2–), 1.69 (2H, m, –CH_2–), 3.82 (6H, s, *p*-OCH_3), 3.83 (6H, s, *o*-OCH_3), 4.14 (2H, t, J = 6.9 Hz, –CH_2–), 6.12 (2H, s, ArH), 8.38 (1H, s, –CH=N–); δ_C 14.1, 22.6, 26.0, 29.1, 29.3, 29.5, 29.6, 31.9, 55.9, 56.2, 74.0, 90.9, 102.9, 117.8, 144.0, 144.2, 160.3, 162.5 (Found: M^+, 379.2729. $C_{22}H_{37}NO_4$ requires M, 379.2722).

Photochemical reactions of oxime ethers in di-*tert*-butyl peroxide

A solution of the oxime ether (0.025 mmol) and DTBP (0.05 mmol) in benzene or cyclohexane, plus any additive (*e.g.* methyl thioglycolate) was degassed by bubbling nitrogen for *ca.* 15 min, and illuminated in a quartz EPR tube (4 mm od) using either a medium pressure 125 W Hg lamp (20 h) or a medium pressure 400 W Hg lamp (6 h). The product mixtures were analysed by GC/MS.

O-Undecyl benzaldoxime **3a** and DTBP illuminated in cyclohexane; peak no. 98, *tert*-butyl alcohol; peak no. 203, benzaldehyde; peak no. 207, benzonitrile; peak no. 336, undecanal, *m*/*z* (relative intensity) 126 (4), 82 (23), 57 (53), 56 (48), 55 (50), 44 (41), 43 (90), 41 (100), 29 (70), 27 (45); peak no. 364, undecanol, 154 ($M^+ - H_2O$) (1), 126 (4), 83 (28), 69 (51), 56 (62), 55 (84), 43 (89), 41 (100), 29 (52); peak no. 596, unreacted **3a**; additional, unidentified peaks were present at large t_R.

The above reaction was carried out using benzoyl peroxide as initiator in refluxing benzene: peak no. 98, *tert*-butyl alcohol; peak no. 199, benzaldehyde; peak no. 213, benzonitrile; peak no. 336, undecanal; peak no. 346, benzoic acid; peak no. 368, undecanol; peak no. 596, unreacted **3a**. When these reactions were repeated using methyl thioglycolate as a polarity reversal catalyst the same products were obtained. Similarly, on using di-*tert*-butyl peroxyoxalate as initiator in refluxing cyclohexane, the same products were obtained.

O-Dodecyl 2,4,6-trimethoxybenzaldoxime **7d** and DTBP were illuminated in benzene; peak no. 98, *tert*-butyl alcohol; peak no. 378, dodecanal, *m*/*z* (relative intensity) 166 (2), 82 (57), 67 (47), 57 (71), 55 (55), 43 (68), 41 (100), 29 (56); peak no. 401, dodecanol, 168 ($M^+ - H_2O$) (1), 140 (4), 97 (11), 83 (26), 69 (36), 56 (48), 55 (90), 43 (79), 41 (100), 29 (62); peak no. 401, 2,4,6-trimethoxybenzonitrile, 193 (M^+) (100), 164 (35), 150 (28), 104 (29), 77 (40), 76 (31), 69 (80), 55 (43), 41 (48), 29 (34); peak no. 556, unreacted **7d**. The mixture also contained unidentified impurities.

O-Dodecyl pentafluorobenzaldoxime **5d** and DTBP were illuminated in benzene; peak no. 98, *tert*-butyl alcohol; peak no. 149, pentafluorobenzonitrile, peak no. 297, dodec-1-ene, 168 (M^+) (5), 84 (24), 70 (63), 69 (43), 57 (38) 56 (58), 55 (100), 43 (80), 41 (89), 27 (70); peak no. 377, dodecanal; peak no. 403, dodecanol; peak no. 502, unreacted **5d**.

O-Undecyl *p*-nitrobenzaldoxime **4a** and DTBP were illuminated in benzene; peak no. 98, *tert*-butyl alcohol; peak no. 340, undecanal; peak no. 367, undecanol; peak no. 585, unreacted **4a**.

Degassed solutions of oxime ethers **3c**–**7c** (~0.025 mmol) in toluene (100 μl) were photolysed for 24 h by light from a 125 W medium pressure Hg lamp and the products analysed by GC/MS. In all cases the alcohols and aldehydes described above were formed.

A solution of *O*-undecyl benzaldoxime **3a** (0.025 mmol) in toluene (0.2 cm^3) was heated for 6 h at 60 °C. GC/MS analysis showed only starting materials.

Photolysis of *O*-pent-4-enyl benzaldoxime 3e: formation of 2-methyltetrahydrofuran

A degassed solution of *O*-pent-4-enyl benzaldoxime **3e** (20 mg) in toluene (300 μl) in a quartz tube was illuminated for 3 h using a 400 W Hg lamp. The product mixture was analysed by GC/MS; peak no. 100, 2-methyltetrahydrofuran, *m*/*z* (relative intensity) 86 (M^+) (12), 71 (100), 45 (24), 43 (95), 42 (70), 41 (98), 39 (28), 27 (35); peak no. 204, benzonitrile; peak no. 382 unreacted **3e**.

Relative kinetic study

Oxime ether **3b** (19.4 mg, 0.12 mmol) in DTBP (0.5 cm^3) was photolysed with unfiltered light from a 500 W super pressure Hg lamp directly in the resonant cavity of the EPR spectrometer. Suitable spectral peaks from the iminyl **13** and adduct radicals **11** were double integrated using the Bruker WINEPR software. Several samples of similar concentration were examined. The relative concentrations of the iminyl and adduct radicals formed from oxime ether **3a** were determined in a similar way. A sample was also dissolved in cyclopropane and the spectra analysed in the same manner.

Acknowledgements

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

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