An electron paramagnetic resonance study of intermediates generated from aromatic aldimines†

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It was shown by EPR spectroscopy that *N*-aryl-imines undergo hydrogen atom abstraction by *tert*-butoxyl radicals to generate imidoyl radicals in competition with addition to the C=N double bond to generate aminyl radicals. The latter were subsequently oxidised to nitroxides (aminoxyls) and also fragmented to release *tert*-butyl radicals and iminyl ethers. The main products identified were imines formed by combination of the imidoyl radicals with other radicals in the system. Thus, hydrogen abstraction is probably the most important homolytic pathway for the precursor imines. A similar reactivity pattern was found for *N*-*tert*-butyl-imines. DFT computations (B3LYP with a 6-31G* basis set) indicated that α-scissions of imidoyl radicals, ArN=C•R (R = *t*-Bu or Me), to produce isonitriles, ArNC, were too endothermic to occur under the present experimental conditions. *tert*-Butoxyl radicals were shown to add to 1-isocyano-4-chlorobenzene to generate *N*-arylimidoyl radicals that fragmented to afford 4-chloro-1-isocyanatobenzene.

Introduction

It was shown recently[1] that *tert*-butoxyl (and other) radicals added rapidly to the C=N bonds of arylaldoxime ethers (ArCH=NOR) to give oxyaminyl radicals (ArCHXN•OR). Simultaneously, abstraction of iminyl hydrogen atoms also took place to yield oximidoyl radicals (ArC•=NOR), *i.e.* radical attack on these substrates was comparatively unselective. Radical reactions of the related oxime esters (ArCH=NOC-(O)R) were complicated by the fact that photo-dissociation of the esters took place. However, aminyl radicals, from additions to the C=N bonds, were spectroscopically detected in several cases.[2]

The situation *vis a vis* the homolytic chemistry of imines was less clear. Danen and West showed that *tert*-butoxyl radicals abstracted a hydrogen atom from aldimines (RCH=NR, R = alkyl) to generate imidoyl radicals (RC•=NR).[3] The EPR spectra of the latter radicals were characterised by small *g*-factors (2.0016) and small N-hyperfine splittings (hfs) [$a(N)$ = 1.2 to 1.9 G]. A series of *N*-*tert*-butylimidoyl radicals was also prepared by reaction of *tert*-butoxyl radicals with the parent *N*-*tert*-butylimines (RCH=NBu-*t*).[4] Related imidoyl radicals were generated by radical addition to alkyl isonitriles[5] and otherwise.[6]

$$RN{\equiv}C: + Z^{\bullet} \longrightarrow RN{=}C^{\bullet}{-}Z \longrightarrow R^{\bullet} + NC{-}Z$$

These *N*-alkylimidoyl radicals were found to readily undergo β-scission to release an alkyl radical together with the corresponding cyanide; for example, at 243 K the rate constant for β-scission of *t*-BuN=C•SiEt₃ was found to be:[5] 1.4×10^5 s⁻¹.

Similar facile β-scission of analogous *N*-arylimidoyl radicals **2** would not be expected because the putative aryl radicals would be σ-radicals and hence thermodynamically destabilised. There seemed a good chance therefore that *N*-arylimidoyl radicals would have longer lifetimes than their *N*-alkyl counterparts and could therefore be spectroscopically detected at higher temperatures and could be incorporated into chemical sequences. Previous research had shown that imidoyl radicals could take part in intermolecular additions to unsaturated substrates,[7] cyclisations,[8] cyclisations onto aromatic rings,[9] and cyclisations onto sulfur.[10] Various heterocyclic rings had been constructed by annulations involving imidoyl radicals and species containing multiple bonds;[11,12] several novel heterocyclic structures had also been made in this way.[11–13] The use of imidoyl radicals generated from isonitriles has recently been reviewed.[14] The research described in this paper was undertaken to examine the homolytic chemistry of *N*-arylimines and related compounds, to test the selectivity of radical generation from them, to try and spectroscopically detect *N*-arylimidoyl radicals and to compare behaviour with other molecules containing C=N double bonds.

Results and discussion

A series of *N*-arylimines [*N*-(neopentylidene)anilines] (**1**) was prepared by reacting pivaldehyde with an aniline using standard methods (Scheme 1).[15,16] Solutions of each imine and di-*tert*-butyl peroxide (DTBP) in *tert*-butylbenzene, cyclopropane or neat peroxide, depending on the desired temperature range, were photolysed with light from a 500 W super pressure Hg lamp in the resonant cavity of an EPR spectrometer. For most of the imines an EPR spectrum developed that consisted of a series of narrow lines ($\Delta H_{pp} \leq 1$ G) clearly showing a N hfs of 12 ± 1.5 G. The spectra were interpreted with the help of computer simulations and the resultant hfs are listed in Table 1. For several of the imines broad singlets ($\Delta H_{pp} \sim 15$ G) were observed at lower temperatures. No fine structure could be resolved even in photolyses carried out at 160 K in cyclopropane solvent.

Alkylimidoyl radicals have σ-electronic configurations[3,4] but spin reaches the N-atom *via* charge separated structures (R¹N⁺•=C⁻R²). There was a possibility that *N*-arylimidoyl radicals (**2**) might have significantly different spin distributions

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i ArSO$_3$H, PhH, reflux

Scheme 1
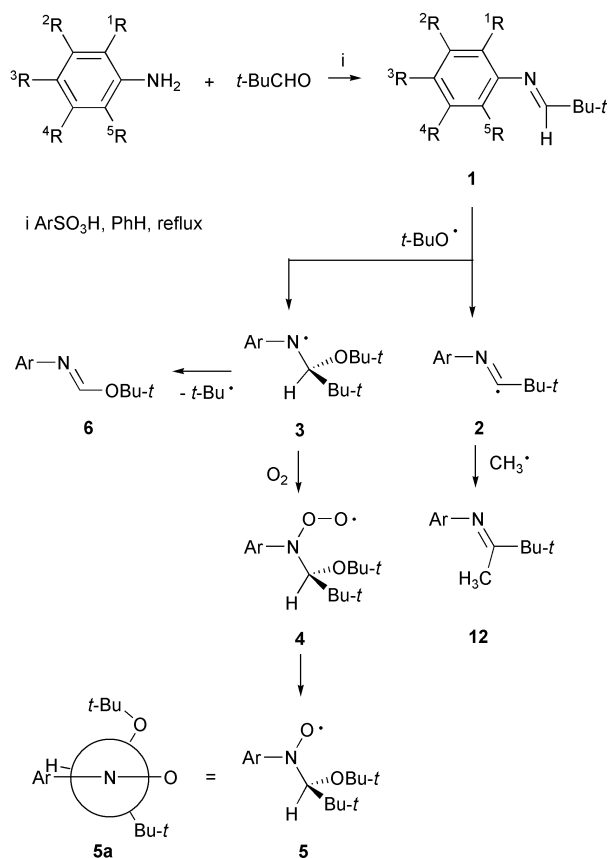
1	^{1}R	^{2}R	^{3}R	^{4}R	^{5}R
a	H	H	H	H	H
b	H	H	Me	H	H
c	H	H	t-Bu	H	H
d	H	H	MeO$_2$C	H	H
e	H	H	MeO	H	H
f	Me	H	H	H	Me
g	H	Me	H	Me	H
h	H	t-Bu	H	t-Bu	H
i	H	MeO	H	MeO	H
j	H	F	H	F	H
k	Me	H	Me	H	Me
l	F	H	F	H	F
m	MeO	H	MeO	H	H
n	H	MeO	MeO	MeO	H

because of electron delocalisation into the aromatic rings. Several model imidoyl radicals were therefore examined by the DFT method. Computations were implemented with the Gaussian 98W software package[17] using the B3LYP method. The main findings are set out in Table 2.

The structures of *N*-alkylimidoyl, *N*-arylimidoyl and *N*-aryl-*C*-arylimidoyl radicals were all computed to be essentially planar. The N=C• bond lengths and the bond angles at the N- and C•-atoms were found to differ only marginally amongst the radical types (Table 2). The computed N-hfs were small, particularly for the larger basis sets and lowest energy computations, and in reasonable agreement with experimental data from *N*-alkylimidoyl radicals.[3,4] Thus, the computations suggested that the electronic structures of *N*-arylimidoyl radicals (**2**) do not differ much from those of *N*-alkyl analogues. The hfs computed for H-atoms of the aromatic rings were also very small (Table 2). Most likely therefore the broad, unresolved signals observed at lower temperatures can be assigned to radicals **2** and the *g*-factors, measured in a couple of cases, (Table 1) tended to confirm this. A similar broad unresolved singlet was previously reported for the related *t*-BuNC•Ph radical.[5]

The well resolved spectra with $a(N) = 12 \pm 1.5$ G were clearly not due to imidoyl radicals. By comparison with previous EPR studies of compounds containing C=N bonds,[1,2] the most likely alternatives were aminyl radicals **3** formed by addition of *t*-BuO• radicals to the iminyl C-atoms. However, literature data for model aminyls[18,19] indicated *g*-factors of 2.0035 to 2.0045, $a(N)$ values in the range 9–11 G and larger hfs for aromatic hydrogen atoms, *e.g.* for PhN•Bu-*t*, $g = 2.0035$, $a(N) = 9.7$ G, $a(H^{2,6}) = 5.8$, $a(H^4) = 7.1$, and $a(H^{3,5}) = 2.0$ G.[20] Comparison with the data in Table 1 indicated that the majority of radicals were not aminyls, although the radical observed from the 4-methoxy-imine **1e** might be the corresponding aminyl **3e**. A significant hfs from the β-hydrogen atom of **3e** would be expected. The line width was *ca.* 2.5 G so that a doublet hfs of < 2 G could have remained unresolved. However, if the radical from **1e** was an aminyl it must have adopted a preferred conformation in which the β-hydrogen was in the nodal plane of the SOMO (see below). It was noteworthy that only one aminyl radical, that from the 4-methoxy-imine **1e** was (probably) detected. Other imines containing MeO substituents (**1i**, **1m** and **1n**) failed to show aminyl or nitroxide signals. Imines **1m,n** showed rapid reaction on mixing with DTBP, before photolysis, and hence non-radical processes could have intervened, effectively blocking the desired radical reactions.

A further possibility was that the majority of the spectra were due to nitroxide radicals (aminoxyls) **5** formed by oxidation of the first formed aminyls. Literature hfs for model nitroxide radicals[18,19] were very close to our data (Table 1) for the N-atoms and ring H-atoms. Reported *g*-factors for aryl alkyl nitroxides are about 2.0060 *i.e.* very close to the *g*-factor measured for the spectrum of this type derived from the imine **1d** (Table 1). We therefore assign all these spectra to the corresponding nitroxides. It is well known[21] that aminyl radicals readily react with dioxygen to give peroxyl radicals **4** and that these in turn are converted to nitroxides by reaction with a second aminyl radical, and/or by reaction with a second peroxyl radical. Although the solutions were deaerated before photolysis, it is difficult to exclude all traces of oxygen, and only very low concentrations of the latter are needed in EPR spectroscopic work because nitroxide radicals are thermodynamically stabilised and have much longer lifetimes than aminyl radicals. Hence, only traces of dioxygen are sufficient to ensure that the species detected by EPR spectroscopy will be nitroxides.

A difficulty with this identification was that none of the spectra revealed hfs from the β-hydrogen present in **5**. However, the α-C-atom of species **5**, to which the β-H-atom is attached, also carries two bulky substituents. These will tend to maximise their distance from the Ar group and O-atom attached to the N-atom of **5**. This will inevitably constrain the β-H-atom to be co-planar with the N–O group and hence in the nodal plane of the SOMO containing the unpaired electron. Structure **5a** depicts the most likely conformation and this is expected to show zero, or near zero, hfs from the β-H-atom. A similar conformation would be expected for the aminyl radical **3e** (see above). Strongly hindered radicals with "invisible" β-H-atoms have been reported previously.[22] Our observations of nitroxide radicals **5** can therefore be taken as good evidence that the initial species formed were the aminyl radicals **3**.

An important feature of the results was the observation of *tert*-butyl radicals (along with nitroxide spectra) from the majority of imines. In principle, *t*-Bu• radicals could be released by α-scission of imidoyl radicals, [eqn. (1), R^2 = *t*-Bu], a process that has already been suggested as feasible, at least when the attacking (or released) species has fair stability.[23,24] To test the viability of this hypothesis DFT computations, B3LYP variant, were implemented using the Jaguar software suite[25] for a series of model imidoyl radicals.
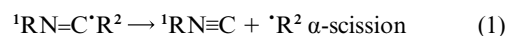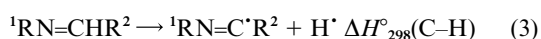
$$^1RN{=}C^{\bullet}R^2 \rightarrow {}^1RN{\equiv}C + {}^{\bullet}R^2 \quad \text{α-scission} \qquad (1)$$

Table 1 Experimental data from photochemical reactions of ArN=CHBu-*t* with DTBP[a,b]

Imine/Ar	Temp./Solvent	Nitroxide 5	Aminyl 3	Imidoyl 2	*t*-Bu	Other info.
1a/Ph	165–210/CP			g 2.0023 ΔH_{pp} 15	Y	
1b/4-MeC$_6$H$_4$	320/DTBP	a(N) 13.1 a(H^{2,6}) 2.7 a(H^{3,5}) 0.9 a(CH$_3$) 1.8	ΔH_{pp} 11			
1c/4-*t*-BuC$_6$H$_4$	290/DTBP	a(N) 12.7 a(H^{2,6}) 2.0 a(H^{3,5}) 0.9			Y	
1d/4-MeO$_2$CC$_6$H$_4$	280/DTBP	g 2.0060 a(N) 11.3 a(H^{2,6}) 2.1 a(H^{3,5}) 1.0			Y	
1e/4-MeOC$_6$H$_4$	160–210/CP & BPh		a(N) 10.7 a(H^{2,6}) 5.0			Broader lines ΔH_{pp} *ca.* 2.5 G Dimer nitroxide obs.
1f/2,6-diMeC$_6$H$_3$	270/DTBP					
1g/3,5-diMeC$_6$H$_3$	240/DTBP			ΔH_{pp} 15	Y	
1h/3,5-di-*t*-Bu-C$_6$H$_3$	290/DTBP	a(N) 12.9 a(H^{2,6}) 1.9 a(H^4) 1.9		ΔH_{pp} 15		
1i/3,5-diMeO-C$_6$H$_3$	240/DTBP			ΔH_{pp} 15 g 2.0015	Y	
1j/3,5-diFC$_6$H$_3$	250/DTBP	a(N) 11.6 a(F^{2,6}) 2.7			Y	
1k/2,4,6-triMe-C$_6$H$_2$	290/DTBP	a(N) 13.1				Mix of benzyl obs. Dimer nitroxide (g 2.0061) also obs.
1l/2,4,6-triF-C$_6$H$_2$	240/DTBP	a(N) 12.4			Y	

[a] Hfs in G; 10 G = 1 mT, CP = cyclopropane, BPh = *tert*-butylbenzene. [b] Imines **1m** and **1n** reacted immediately on dissolving in DTBP and no spectra were obtained.

Table 2 DFT computational results for model imidoyl radicals

Radical	Method//Geom.	Energy/ Hartrees	C=N/Å	C$_{Ar}$NC$^\bullet$ NC$^\bullet$C/deg	a(N)/G	a(R^2)/G	a(R^1)/G
MeNC$^\bullet$Me	UHF/B3LYP/6-31G//UHF/B3LYP/6-31G	−172.553188	1.249	128.1 129.4	4.9	C–CH$_3$ 0.8	N–CH$_3$ 8.9
MeNC$^\bullet$Me	UHF/B3LYP/6-311G(d,p)//UHF/B3LYP/ 6-311G(d,p)	−172.657999			0.8	C–CH$_3$ 0.1	N–CH$_3$ 12.5
PhNC$^\bullet$Me	UHF/B3LYP/6-31G//UHFB3LYP/6-31G	−364.255570	1.254	129.5 129.4	5.4	^{o}H 0.0 ^{m}H 0.5 ^{p}H 0.3	N–CH$_3$ 9.5
PhNC$^\bullet$Me	UHF/B3LYP/6-31G+//UHFB3LYP/6-31G	−364.271247			4.4	^{o}H 0.2 ^{m}H 0.5 ^{p}H 0.3	N–CH$_3$ 10.8
PhNC$^\bullet$Me	UHF/B3LYP/6-311G//UHFB3LYP/6-311G	−364.335933	1.249	130.6 129.5	2.0	^{o}H −0.1 ^{m}H 0.5 ^{p}H 0.3	N–CH$_3$ 8.8
PhNC$^\bullet$Me	UHF/B3LYP/6-311G(2d,p)//UHFB3LYP/6-311G	−364.454109			1.9	^{o}H −0.1 ^{m}H 0.6 ^{p}H 0.3	N–CH$_3$ 8.7
PhNC$^\bullet$Ph	UHF/B3LYP/6-31G//UHF/B3LYP/6-31G	−555.955774	1.260	130.0 129.5	5.7	^{o}H 0.0 ^{m}H 0.5 ^{p}H 0.3	^{o}H −0.4 ^{m}H 0.9 ^{p}H 0.0
PhNC$^\bullet$Ph	UHF/B3LYP/6-311+(d,p)//UHF/B3LYP/6-31G	−556.229910			2.3	^{o}H 0.1 ^{m}H 0.5 ^{p}H 0.3	^{o}H −0.6 ^{m}H 1.0 ^{p}H −0.1
MeNC$^\bullet$Ph	UHF/B3LYP/6-31G//UHF/B3LYP/6-31G	−364.252210	1.252	128.6 129.4	5.4	CH$_3$ 1.3	^{o}H −0.5 ^{m}H 0.9 ^{p}H 0.0

$$^1RN=C^\bullet R^2 \rightarrow {}^1R^\bullet + N\equiv CR^2 \quad \beta\text{-scission} \qquad (2)$$

$$^1RN=CHR^2 \rightarrow {}^1RN=C^\bullet R^2 + H^\bullet \quad \Delta H°_{298}(\text{C–H}) \qquad (3)$$

The results (Table 3) showed that β-scission was exothermic for *t*-BuN=C$^\bullet$Bu-*t* and only mildly endothermic for *t*-BuN= C$^\bullet$Ph and even for MeN=C$^\bullet$Me. This was in good accord with the experimental observations of facile alkyl radical release by *N*-alkylimidoyls.[5] On the other hand, the DFT computations indicated that α-scission was strongly endothermic for PhN=

C$^\bullet$Bu-*t* and other imidoyls (Table 3). In view of these results, it seems unlikely that the *t*-Bu$^\bullet$ radicals, detected during the imine/DTBP photolyses, were formed by this route.

The most likely source of the *t*-Bu$^\bullet$ radicals appears to be β-scission of the aminyl radicals **3**. Release of *t*-Bu$^\bullet$ from **3** would afford the iminyl ethers **6** (Scheme 1) in a process likely to be energetically favourable. This fragmentation of **3** presumably competed successfully with nitroxide formation in most cases because of the very low oxygen pressures.

Dilute solutions (*ca.* 5 mg in 0.5 cm^3 DTBP) of the 2,6-dimethyl- (**1f**) and 2,4,6-trimethyl-imines (**1k**) showed broad,

Table 3 DFT Computations of thermodynamic parameters for imidoyl and related species.[a,b]

Imidoyl radical	α-Scission ΔH°_{298}(B3LYP)/kcal mol^{-1}	β-Scission ΔH°_{298}(B3LYP)/kcal mol^{-1}	ΔH°_{298}(C–H)[c]/kcal mol^{-1}
MeN=C˙Me	31.0	7.0	87.5
t-BuN=C˙Bu-*t*	17.0	−2.2	90.9
PhN=C˙Me	27.4		91.0
PhN=C˙Bu-*t*	20.9		91.9
t-BuN=C˙Ph		6.4	92.5
PhN=C˙Ph			93.9

[a] B3LYP method employing the 6-31G* basis set implemented with the Jaguar software suite;[25] frequencies were scaled by 0.9614.[26] [b] H°_{298} (B3LYP)/ Hartree for individual species were: H, −0.500272; CH$_3$˙, −39.800170; *t*-Bu˙, −157.671038; CH$_3$CN, −132.703166; CH$_3$NC, −132.664946; MeN= C˙Me, −172.514472; MeN=CHMe, −173.154158; PhNC, −324.345700; PhCN, −324.380040. [c] B3LYP computed C–H bond dissociation energies of the corresponding imines.

Table 4 EPR parameters of long-lived radicals (**8**) derived from di- and tri-methyl imines.[a]

Precursor	Temp./K	*g*-Factor	$a(N_1)$	$a(N_2)$	$a(6H)$
2,6-diMeC$_6$H$_3$ (**1f**)	270	—	8.70	3.53	0.48
2,4,6-triMeC$_6$H$_2$ (**1k**)	300	2.0061	8.82	3.55	0.51

[a] Spectra in DTBP solution, hfs in G.

unresolved, nitrogen triplets from nitroxides. Dilute samples of **1k** in *tert*-butylbenzene, on prolonged photolysis to quench the nitroxides, showed weak spectra consisting of at least 27 narrow lines with a spacing of 1.7 G. Comparison with literature data for 2- and 4-methylbenzyl radicals indicated that this spectrum was probably a mixture of isomeric dimethylbenzyl radicals formed by H-abstraction from the two types of methyl groups in the aromatic ring. Analogous benzyl radicals were not observed when **1f** or **1b** was photolysed under similar conditions. However, weak and easily saturated benzyl spectra would be difficult to detect in the presence of nitroxides so abstraction of the benzyl hydrogen atoms from these molecules should not be ruled out.

Photolyses of more concentrated solutions of **1f** and **1k** (50 mg in 0.5 cm³ DTBP) led to unusual spectra (Fig. 1) that were
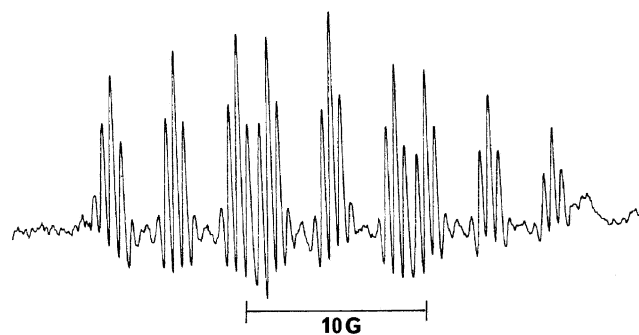

Fig. 1 9.1 GHz EPR spectrum obtained from imine **1k** in neat DTBP on photolysis at 298 K. The spectrum is shown in 2nd derivative presentation.

long-lived. These spectra were readily analysed and simulated and had hfs (Table 4) from two non-equivalent N-atoms. The *g*-factor was measured for one of these radicals (Table 4) and this indicated they were also nitroxides. The most likely explanation of their formation is shown in Scheme 2. Initially formed aminyl radicals (**3f,k**) could add to a second molecule of imine, at the higher concentrations employed, producing new aminyl radicals **7** that were subsequently oxidised to nitroxides **8** containing β-nitrogen atoms. The reason these dimer-nitroxides were only observed from imines **1k,f** will be because of the extra
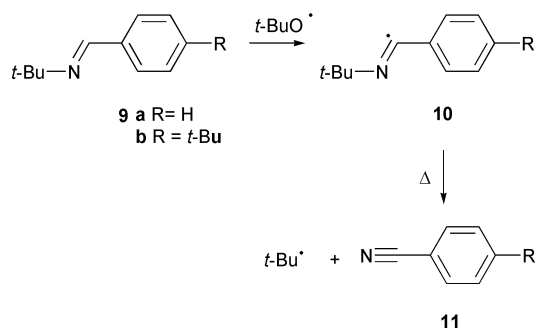

Scheme 2
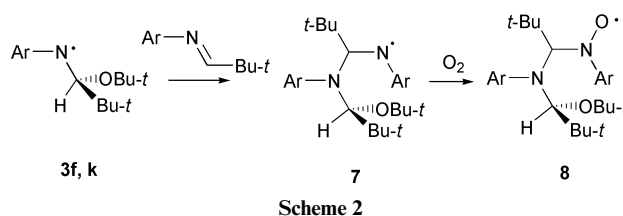
lifetime conferred on them by steric shielding from the 2,6-dimethyl groups in the aromatic rings.

For comparison purposes, radical generation from two *N*-(benzylidene)-*tert*-butylamines **9a,b** was examined under similar conditions. Both imines gave rise to broad signals at low temperatures, similar to that reported by Roberts and co-workers,[5] that we assign to imidoyl radicals **10**. Accompanying this were, in each case, small triplets [*g* = 2.0007, *a*(2H) = 1.25 G from **9a**, and 1.15 G from **9b**] and these clearly belong to the corresponding arylacyl radicals, ArC˙O, presumably formed by H-abstraction from the corresponding aldehydes (see below). At higher temperatures (*T* > 270 K) the spectrum of the *t*-Bu˙ radical was also observed in both systems. This is consistent with fragmentation of the imidoyl radicals to afford nitriles **11**.

End product analyses were carried out by GC–MS for selected reactions in order to shed more light on the mechanisms. The reaction of the *p*-tolyl-imine **1b** with DTBP produced ethane, isobutene, isobutane (both traces only), pivaldehyde, *p*-toluidine and imine **12b** as well as some minor unidentified components. In neat DTBP the main fate of reactive radicals is likely to be coupling or disproportionation, because of the absence of good H-donors. At the photolysis temperature the initial *t*-BuO˙ radical will undergo some β-scission to generate methyl radicals. This accounts for the formation of ethane. The isobutene and isobutane result from combination and disproportionation of *t*-Bu˙ radicals released on β-scission of aminyl radicals **3b** (Scheme 1). The initial imine was highly purified and therefore the formation of pivaldehyde and toluidine indicates that some hydrolysis occurred under the experimental conditions. The formation of **12b** can be accounted for by combination of an imidoyl radical **2b** with a methyl radical (Scheme 1). No trace of 4-MeC$_6$H$_4$NC was found and this confirmed that α-scission of the imidoyl radicals did not occur.

The only product identified from the reaction of the *N-tert*-butyl-imine **9b** was the nitrile **11b** and this confirmed that the major process in this case was imidoyl formation followed by β-scission (Scheme 3). Isobutene and isobutane from coupling

Scheme 3

of the released *t*-Bu˙ radicals were probably present but could not be identified with certainty because of overlap with added solvent.

Imidoyl radicals have frequently been generated by radical addition to isonitriles (see above). An attempt was made, therefore, to generate an imidoyl radical from 4-chlorobenzoisonitrile **13**. No spectra were observed on photolysis of solutions of **13** in DTBP. However, GC–MS analysis showed that 4-chloro-1-isocyanatobenzene **15**, and its hydrolysis product, 4-chloroaniline, were formed, together with isobutene and isobutane. Most likely addition of a *t*-BuO˙ radical to the isonitrile generates imidoyl radical **14** that rapidly undergoes β-scission to afford **15** and a *t*-Bu˙ radical (Scheme 4). This experiment supported our conclusion (above) that the
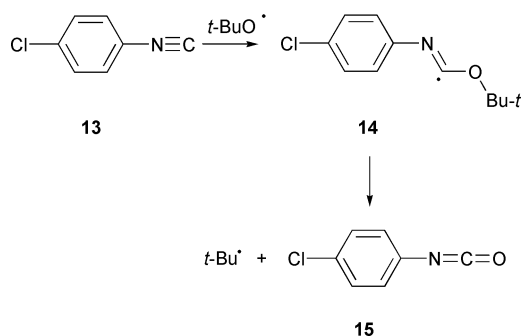
Scheme 4

reaction with imine **1b** did not yield tolyl isonitrile, otherwise we should have detected tolyl isocyanate. This was additional evidence that the α-scission process of imidoyl radicals did not participate under these conditions.

Photolyses of several diarylimines (ArN=CHAr, Ar = Ph, 4-*t*BuC$_6$H$_4$) in DTBP were also examined by EPR spectroscopy. Spectra of transient radicals were obtained in several cases but these did not correspond to imidoyl, aminyl or nitroxide radicals; efforts to rationalise these spectra are continuing.

Conclusions

EPR experiments showed that *t*-BuO˙ radicals abstracted iminyl H-atoms from *N*-aryl imines (**1**) to generate imidoyl radicals **2**. At the same time, addition to the C=N double bond took place to generate aminyl radicals **3** that were subsequently oxidised to nitroxides **5** and underwent β-scission releasing *t*-Bu˙ radicals together with iminyl ethers **6**. When the *N*-aryl-imines **1f** and **1k** were used at higher concentrations, the aminyl radicals added to more imine leading to the formation of "dimer" nitroxides **8** with two non-equivalent N-atoms.

Although the EPR spectra were usually dominated by nitroxides, this was not a good indication of the relative importance of abstraction and addition reactions of the imines. Such nitroxides are persistent so that their concentration builds up, in comparison with the transient imidoyl radicals, giving a

misleading impression from the relative spectral intensities of the two types of species. The product analyses are more reliable in this instance. For imine **1b** neither nitroxides, nor their disproportionation products, were detected. Similarly, no amines or coupling products from the aminyl radicals **3b** were observed and the isobutene and isobutane, derived from the *t*-Bu˙ radicals released from **3b**, were trace products only. On the other hand, the imine **12b** was the major product. This was a good indication that H-abstraction from **1** was actually the major process. Further evidence suggesting that radical addition to the C=N bond was of minor importance came from EPR experiments in which Ph˙ and/or PhCO$_2$˙ radicals (from dibenzoyl peroxide), PhS˙ radicals (from diphenyl disulfide), Me$_3$Sn˙ radicals (from hexamethylditin) and Et$_3$Si˙ radicals (from Et$_3$SiH–DTBP) were generated in the presence of imine **1b**. Neither aminyl radicals, nor the corresponding nitroxides, were detected by EPR spectroscopy in any of these systems. A similar reactivity pattern was found for the *N-tert*-butyl-imines **9**. No evidence, either from EPR spectroscopy or from end product analysis, was found of *t*-BuO˙ addition. Rather, the dominant H-abstraction reaction gave imidoyl radical **10** that subsequently fragmented.

Experiments with isonitrile **13** provided further evidence of the difficulty of detecting *N*-arylimidoyl radicals by EPR spectroscopy. Radical **14** was not observed, although end product analysis suggested that it had formed and fragmented by β-scission to give isocyanate **15**.

Experimental

Quantum chemical calculations

Quantum chemical calculations were carried out with the Gaussian 98W package[17] and/or for larger species (see Table 3) the Jaguar[25] software suite was used. For the most part density functional theory, B3LYP variant, was employed. For closed shell molecules the RHF formalism was employed and for open shell radicals UHF formalism was applied. The equilibrium geometries were fully optimised with respect to all the geometric variables, no symmetry being assumed, with 6-31G, 6-31G* and 6-311G basis sets; for the more extensive basis sets the geometries used are listed in Table 2. Final $\langle S^2 \rangle$ values of ≤ 0.756 were obtained for each radical indicating negligible contamination by higher spin states. Isotropic hfs for the imidoyl radicals were obtained from Fermi contact integrals as listed in the Gaussian 98 output. For the calculation of thermodynamic properties the computed vibrational frequencies were scaled by the recommended[26] factor of 0.9614.

General

^{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). EPR spectra were obtained with Bruker ER 200D and EMX 10/12 spectrometers operating at 9 GHz with 100 kHz modulation. Samples of the substrate (0.3 to 40 mg) and di-*tert*-butyl peroxide (0.01 to 0.5 cm^3), sometimes in *tert*-butylbenzene (0.5 cm^3) as solvent, in 4 mm od quartz tubes, 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. In all cases where spectra were obtained, hfs were assigned with the aid of computer simulations using Bruker SimFonia software.

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 CaH₂. 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). N-(2,2-Dimethylpropylidene)aniline (91%) (**1a**),[27] N-(2,2-dimethylpropylidene)-4-methoxycarbonylaniline (78%) (**1d**),[28] N-(2,2-dimethylpropylidene)-2,6-dimethylaniline (88%) (**1f**),[29] and N-benzylidene-1,1-dimethylethylamine (80%) (**9a**),[16] were prepared as described in the literature.

General procedure for the preparation of N-(2,2-dimethylpropylidene)anilines

Pivaldehyde (1.29 g, 15 mmol) and the aromatic amine (10 mmol) in benzene (16 cm³) containing toluene-p-sulfonic acid (ca. 10 mg) were refluxed in a Dean Stark apparatus until the expected quantity of water had collected. Solvent and excess pivaldehyde were evaporated, and the imines were purified by distillation or crystallisation.

N-(2,2-Dimethylpropylidene)-p-toluidine (1b). 85%, bp 94–96 °C/20 Torr, δ_H 1.22 (9H, s, C(CH₃)₃), 2.35 (3H, s, CH₃), 6.94 and 7.15 (4H, AA′BB′, ArH), 7.70 (1H, s, N=CH); m/z (%), 175 (M⁺, 15), 160 (15), 119 (12), 118 (97), 91 (100), 90 (12). (Found: M⁺, 175.1363. C₁₂H₁₇N requires M, 175.1361. Found: C, 82.3; H, 9.8; N, 7.8. Calc. for C₁₂H₁₇N: C, 82.2; H, 9.8; N, 8.0%).

N-(2,2-Dimethylpropylidene)-4-(1,1-dimethylethyl)aniline (1c). 79%, bp 80–82 °C/0.7 Torr, δ_H 1.23 (9H, s, C(CH₃)₃), 1.37 (9H, s, C(CH₃)₃), 7.01, 7.37 (4H, AA′BB′, ArH), 7.75 (1H, s, N=CH). (Found: M⁺ 217.1822. C₁₅H₂₃N requires M 217.1830. Found: C, 82.9; H, 10.7; N, 6.5. Calc. for C₁₅H₂₃N: C, 82.9; H, 10.7; N, 6.4%).

N-(2,2-Dimethylpropylidene)-3,5-dimethylaniline (1g). 89%, bp 92–94 °C/0.7 Torr, δ_H 1.23 (9H, s, C(CH₃)₃), 2.35 (6H, s, ArCH₃), 6.67 (2H, m, ArH), 6.85 (1H, m, ArH), 7.73 (1H, s, N=CH). (Found: M⁺ 189.1511. C₁₃H₁₉N requires M 189.1517. Found: C, 82.5; H, 10.2; N, 7.4. Calc. for C₁₃H₁₉N: C, 82.5; H, 10.1; N, 7.4%).

N-(2,2-Dimethylpropylidene)-3,5-bis(1,1-dimethylethyl)aniline (1h). 60%, mp 88–89 °C, δ_H 1.20 (9H, s, C(CH₃)₃), 1.35 (18H, s, ArC(CH₃)₃), 6.84 (2H, d, J 1.7 Hz, ArH), 7.24 (1H, t, J 1.7 Hz, ArH), 7.72 (1H, s, N=CH). (Found: M⁺ 273.2460. C₁₉H₃₁N requires M 273.2456. Found: C, 83.4; H, 11.3; N, 5.1. Calc. for C₁₉H₃₁N: C, 83.5; H, 11.4; N, 5.1%).

N-(2,2-Dimethylpropylidene)-3,5-dimethoxyaniline (1i). 65%, bp 108–110 °C/1 Torr, δ_H 1.18 (9H, s, C(CH₃)₃), 3.79 (6H, s, OCH₃), 6.16 (2H, d, J 2.2 Hz, ArH), 6.28 (1H, t, J 2.2 Hz, ArH), 7.69 (1H, s, N=CH). (Found: M⁺ 221.1419. C₁₃H₁₉NO₂ requires M 221.1416. Found: C, 70.5; H, 8.6; N, 6.4. Calc. for C₁₃H₁₉NO₂: C, 70.6; H, 8.65; N, 6.3%).

N-(2,2-Dimethylpropylidene)-3,5-difluoroaniline (1j). 98%, bp 86–87 °C/0.5 Torr, δ_H 1.17 (9H, s, C(CH₃)₃), 6.42–6.68 (3H, m, ArH), 7.65 (1H, br s, N=CH). (Found: M⁺ 197.1010. C₁₁H₁₃F₂N requires M 197.1016. Found: C, 67.0; H, 6.5; N, 7.1. Calc. for C₁₁H₁₃F₂N: C, 67.0; H, 6.6; N, 7.1%).

N-(2,2-Dimethylpropylidene)-2,4-dimethoxyaniline (1m). 68%, bp 100–101 °C/0.5 Torr, δ_H 1.17 (9H, s, C(CH₃)₃), 3.75 (3H, s, OCH₃), 3.77 (3H, s, OCH₃), 6.39 (1H, dd, J 8.2, 2.4 Hz, ArH), 6.45 (1H, d, J 2.4 Hz, ArH), 6.72 (1H, d, J 8.2 Hz, ArH), 7.76 (1H, s, N=CH). (Found: M⁺ 221.1421. C₁₃H₁₉NO₂ requires: M 221.1416. Found: C, 70.5; H, 8.7; N, 6.2. Calc. for C₁₃H₁₉NO₂: C, 70.6; H, 8.7; N, 6.3%).

N-(2,2-Dimethylpropylidene)-2,4,6-trimethylaniline (1k). 73%, bp 71–73 °C/0.7 Torr, δ_H 1.20 (9H, s, C(CH₃)₃), 2.02 (6H, s, ArCH₃), 2.23 (3H, s, ArCH₃), 6.78 (2H, s, ArH), 7.45 (1H, s, N=CH). (Found: M⁺ 203.1670. C₁₄H₂₁N requires M 203.1674. Found: C, 82.7; H, 10.4; N, 6.9. Calc. for C₁₄H₂₁N: C, 82.7; H, 10.4; N, 6.9%).

N-(2,2-Dimethylpropylidene)-2,4,6-trifluoroaniline (1l). 85%, bp 36–38 °C/0.7 Torr, δ_H 1.20 (9H, s, C(CH₃)₃), 6.55–6.77 (2H, m, ArH), 7.83 (1H, br s, N=CH). (Found: M⁺ 215.0918. C₁₁H₁₂F₃N requires M 215.0922. Found: C, 61.4; H, 5.7; N, 6.6. Calc. for C₁₁H₁₂F₃N: C, 61.4; H, 5.6; N, 6.5%).

N-(2,2-Dimethylpropylidene)-3,4,5-trimethoxyaniline (1n). 72%, bp 120–122 °C/0.7 Torr, δ_H 1.15 (9H, s, C(CH₃)₃), 3.77 (3H, s, OCH₃), 3.81 (6H, s, OCH₃), 6.23 (2H, s, ArH), 7.68 (1H, s, N=CH). (Found: M⁺ 251.1519. C₁₄H₂₁NO₃ requires M 251.1521. Found: C, 66.9; H, 8.5; N, 5.5. Calc. for C₁₄H₂₁NO₃: C, 66.9; H, 8.4; N, 5.6%).

N-[4-(1,1-Dimethylethyl)benzylidene]-1,1-dimethylethylamine (9b). This was prepared by a similar method, 79%, bp 130–132 °C/1 Torr, δ_H 1.30 (9H, s, C(CH₃)₃), 1.35 (9H, s, C(CH₃)₃), 7.45 and 7.72 (4H, AA′BB′, ArH), 8.28 (1H, s, N=CH). Found: M⁺ 217.1835. C₁₅H₂₃N requires M 127.1830. Found: C, 82.8; H, 10.7; N, 6.5. Calc. for C₁₅H₂₃N: C, 82.9; H, 10.7; N, 6.4%).

Photochemical reaction of 1b with DTBP

A solution of N-(2,2-dimethylpropylidene)-p-toluidine (40 mg, 0.23 mmol) in DTBP (0.2 cm³) in a quartz tube was deaerated by purging with nitrogen for 15 min and then photolysed with light from a 500 W super pressure Hg lamp for 5.5 h at 300 K. Besides starting materials, and products from DTBP decomposition, the following products were observed: peak no. 90; ethane, peak no. 92; isobutene, peak no. 94; isobutane, peak no. 110; pivaldehyde, peak no. 657; toluidine, peak no. 925; m/z (%) 189 (4), 177 (13), 162 (5), 132 (10), 120 (100), 106 (20), 91 (23), 77 (19), 65 (22), probably N-(1,2,2-trimethylpropylidene)-p-toluidine (**12b**). Careful search was made for 4-methylbenzonitrile and 1-isocyano-4-methylbenzene, but neither was detected.

Photochemical reaction of 9b with DTBP

N-(4-tert-Butylbenzylidene)-tert-butylamine (23.2 mg, 0.11 mmol) was dissolved in DTBP (0.5 cm³) in a quartz tube, deaerated by purging with nitrogen for 15 min, and photolysed with light from a 500 W super pressure Hg lamp for 1 h at 320 K. Besides starting materials, and products from DTBP decomposition, the only significant product shown by GC–MS was 4-tert-butylbenzonitrile. Isobutene and isobutane were obscured by added solvent.

Photochemical reaction of 1-isocyano-4-chlorobenzene with DTBP

A solution of the isonitrile (20 mg, 0.14 mmol) in DTBP (300 cm³) was deaerated by purging with nitrogen for 15 min and then photolysed with light from a 500 W super pressure Hg lamp for 4.5 h at 330 K. GC–MS analysis showed unchanged reactants, and DTBP decomposition products, together with the following products. Peak 85; ethane, peak 88; isobutene, peak 90; isobutane, peak 715; 1-isocyanato-4-chlorobenzene, peak 769; 4-chloroaniline together with minor unidentified components.

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