Thermal decomposition of *tert*-butyl *ortho*-(phenylsulfanyl)- and *ortho*-(phenylsulfonyl)phenyliminoxyperacetates: The reactivity of thio-substituted iminyl radicals

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Received (in Cambridge, UK) 6th December 2000, Accepted 27th February 2001
First published as an Advance Article on the web 12th April 2001

Some *ortho*-(phenylsulfanyl)- and *ortho*-(phenylsulfonyl)-substituted phenyliminyl radicals have been generated by thermal decomposition of suitable *tert*-butyl iminoxyperacetates. The sulfanyl-substituted iminyls showed no tendency to give either 1,7- or 1,6-ring closure onto the *S*-phenyl ring. They gave instead 1,5-cyclisation onto the sulfur atom with release of a phenyl radical and formation of benzoisothiazoles. This seems to be the first example of S_Hi reaction of a nitrogen-centred radical at a sulfide moiety. On the other hand, the sulfonyl-substituted iminyl underwent 1,6-cyclisation to a small extent, furnishing a phenanthridine through an unprecedented 1,5-aryl radical migration from sulfur to nitrogen followed by loss of sulfur dioxide and ring closure of an aryl radical.

Introduction

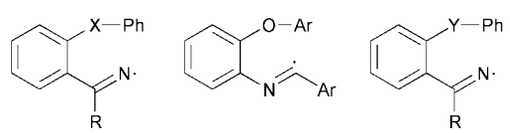
In the last decade, radical reactions have been conclusively accepted as a powerful tool in organic synthesis, and the excellent control of the regio- and stereoselectivity achieved in radical chemistry has allowed an extraordinary growth in the design of novel, exciting radical-based synthetic strategies.[1]

Among the diverse radical species, iminyl radicals were almost entirely ignored by organic chemists until the eighties;[2] however, by now they have been definitely established – by the work of Forrester,[3] McNab,[4] and Zard[5] – as very interesting, versatile intermediates, capable of being employed in many synthetically useful transformations.[6]

Iminyl radicals can be generated by many different techniques, *i.e.* pyrolytic or photochemical reactions,[3,4,6b,d] addition of carbon radicals to nitriles,[6c,e,g–m,r–t] reduction of *N*-chloro ketimines,[2a] hydrogen abstraction from imines,[2c] one-electron reduction of ketoxime esters,[5m] sulfanyl-radical addition to vinyl azides,[6q] Hudson-type reaction of oximes,[6v] and reactions of tin radicals with oxime benzoates,[5f,h,i] sulfenimides,[5e,i] xanthic hydrazones,[5g,i–k] Barton esters[5c,e,i] or benzotriazolylimines.[6n] As far as their applications are concerned, a great deal of work has been done on their intramolecular capture by an olefin moiety: this is a particularly efficient synthetic method for nitrogen heterocycles, especially relevant to the field of alkaloids.[5] However, other interesting behaviours have been reported, *e.g.* addition to aromatic rings[3,4] and fragmentation to nitriles with concomitant opening of strained rings: the latter is a particularly useful process that can be incorporated in synthetically useful radical cascade reactions.[5]

In previous studies, we have focussed our attention on the reactivity of aryliminyl radicals **1**, bearing an *ortho*-aryloxy or arylamino group. These radicals were studied both in solution, when generated by thermal decomposition of suitable *tert*-butyl aryliminoxyperacetates,[7a] and in the gas phase, when produced by flash vacuum pyrolysis (FVP) of appropriate oxime ethers.[7b,c,8]

In solution, all of the iminyls **1** have been found to be unable to give seven-membered cyclisation, contrary to what was previously observed for the oxygenated imidoylic species **2**.[9a,b]



1 **2** **3**

X = O, NH, NMe, NPh;
R = H, Me, Ph

a: Y = S, R = H; **c**: Y = S, R = Ph;
b: Y = S, R = Me; **d**: Y = SO_2, R = Me

However, similar to radicals **2**, some of them (**1**; X = NPh) gave aromatic homolytic substitution through 1,6-spirocyclisation and subsequent 1,5-migration of the phenyl ring from the aminic nitrogen to the iminic one; this was the first reported example of a 1,5-aryl radical migration between two nitrogen atoms.

Considering that the behaviour of imidoyl radicals **2** can be deeply altered by replacing oxygen (or nitrogen) with sulfur, which can undergo an intramolecular S_Hi reaction yielding benzothiazole derivatives,[9c] we addressed our further studies to the sulfur-containing iminyl radicals **3**. In particular, we were interested in investigating the occurrence of a 1,5-aryl radical migration from sulfur to nitrogen together with the possibility of a still unknown S_Hi reaction of the iminyl radical onto the sulfide moiety. This study was undertaken both in solution and in the gas phase (see the accompanying paper[8]).

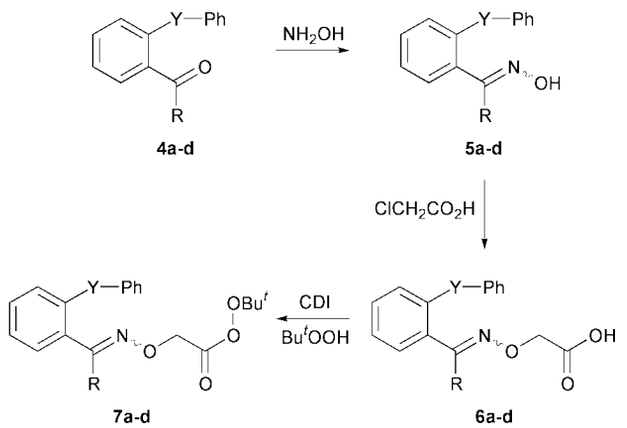
Results and discussion

Although the sulfenimide method of iminyl generation has been most often employed for synthetic purposes, it has been reported that sulfenimides of aromatic ketones are not readily accessible.[10] Therefore, as in the previous paper and according to the method of Forrester,[3] we decided to generate the iminyls **3** by thermal decomposition of suitable *tert*-butyl iminoxyperacetates.

The peracetates **7a**–**d** were prepared from the corresponding carbonyl compounds **4a**–**d** according to the literature method.[3] However, contrary to Forrester's method, the final esterification

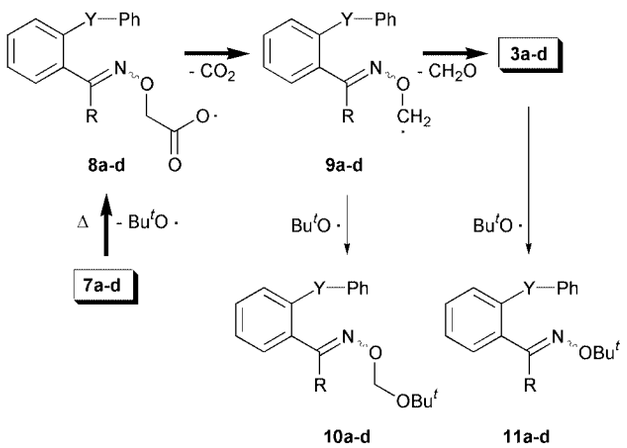
 DOI: 10.1039/b009843o

step was carried out by direct treatment of the acids with *tert*-butyl hydroperoxide and *N*,*N*′-carbonyldiimidazole (CDI) (Scheme 1), without previous conversion of the acids into acyl halides.



Scheme 1

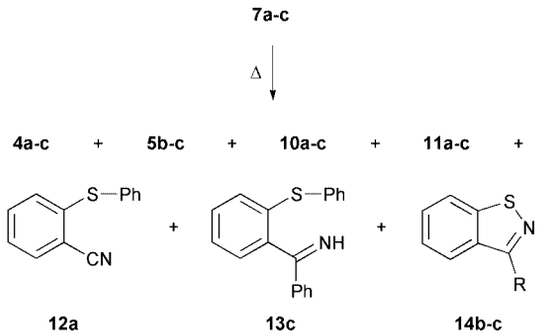
Thermal decomposition of the peresters **7a**–**d** furnishes the corresponding iminyls **3a**–**d** according to Scheme 2.



Scheme 2

As before,[7a] the experiments were carried out in boiling 0.02 M bromobenzene solutions. Under these conditions, the loss of formaldehyde from radicals **9a**–**d** is fast enough to minimise the formation of compounds **10a**–**d**, arising from cage recombination between **9a**–**d** and *tert*-butoxyl radicals.

Decompositions of peresters **7a**–**c** gave the compounds shown in Scheme 3. The formation of iminoacetals **10** (13–24%) has been already discussed above, and that of *O*-*tert*-butyl oximes **11** (traces–7%) can be analogously explained in terms of coupling between iminyls **3** and *tert*-butoxyl radicals (Scheme 2). The carbonyl compounds **4a**–**c** are probably the result of hydrolysis of the corresponding imines **13a**–**c**, which can reasonably derive from iminyls **3a**–**c** by hydrogen abstraction. Support to this hypothesis was given by separation of imine **13c** (16%) from the decomposition mixture of perester **7c**. On the other hand, **4a**–**c** cannot arise from hydrolysis of other imine derivatives, *e.g.* **5a**–**c**, **10a**–**c** or **11a**–**c**, because these compounds are completely stable under chromatographic conditions. Isolation of imines like **13c** has been already reported and discussed in our previous paper.[7a] As stated in that work, the particular, unexpected stability of these derivatives towards chromatographic work-up could be explained both through extensive conjugation (only the compound with R = Ph was isolated) and by an intramolecular hydrogen bonding between nitrogen and sulfur, although, in principle, this interaction is less efficient than in the oxygenated analogues. It still remains

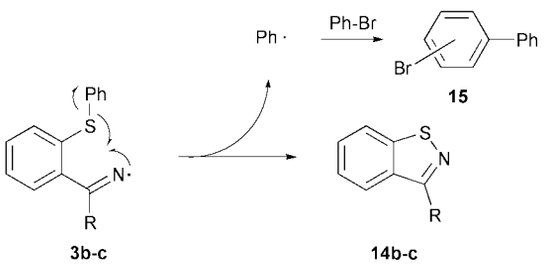


Scheme 3

rather obscure which species acts as a hydrogen donor for iminyls **3**.

The oximes **5b**,**c** (4–10%) could be the result of an oxidation process of the corresponding iminyl radicals, whereas nitrile **12a** (5%), isolated only when R = H, can be easily rationalised by an assisted β-fragmentation of the C–H bond of iminyl **3a**.

By far the most noteworthy compounds separated from the reaction mixtures were the benzoisothiazoles **14b**,**c** (18–25%). The formation of these derivatives can be easily explained by an intramolecular homolytic substitution (S_Hi reaction) at the sulfur atom by the iminyl radical, as shown in Scheme 4.



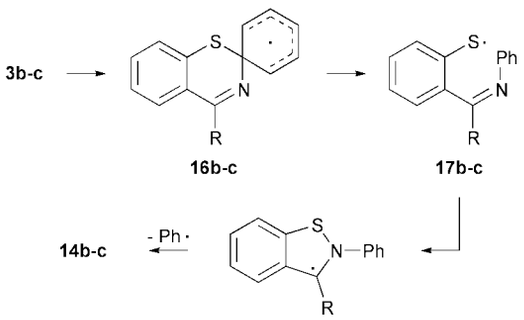
Scheme 4

This behaviour is similar to that observed for analogous imidoyl radicals,[9c] but, to our knowledge, it is the first example of homolytic substitution at the sulfur atom of a sulfide moiety by a nitrogen-centred radical. This is a particularly noteworthy result, since it appears that the formation of the aromatic 5-membered isothiazole ring is a driving force strong enough to release a high-energy phenyl radical with concomitant formation of a sulfur–nitrogen bond, whose strength is definitely lower than that of the sulfur–carbon bond formed in the case of imidoyls.[9c,11]

The presence of phenyl radicals was unquestionably revealed by isolation of the three isomeric bromobiphenyls **15** in about the same overall yield as **14** and in proportions identical with those reported for the homolytic phenylation of bromobenzene with dibenzoyl peroxide.[12] The formation of isothiazoles was also the main product-forming pathway of iminyl radicals in the gas phase (see the accompanying paper[8]).

Taking into account the previous results obtained in solution with some nitrogen-containing iminyl radicals **1** (X = NPh),[7a] an alternative mechanism could nevertheless be envisaged for the formation of isothiazoles **14**. This is based on the possibility of 1,6-spirocyclisation of iminyls **3** with concomitant 1,5-migration of the phenyl group from sulfur to nitrogen through the spirocyclohexadienyl radical **16** (Scheme 5). The resulting thiophenoxyl radical **17** could then cyclise in a 1,5-fashion onto the iminic moiety to give the isothiazole **14**. This mechanism also entails loss of a phenyl radical, although at a different step from that reported in Scheme 4; therefore the confirmed intermediacy of phenyl radicals does not let us discriminate between the two possible pathways.

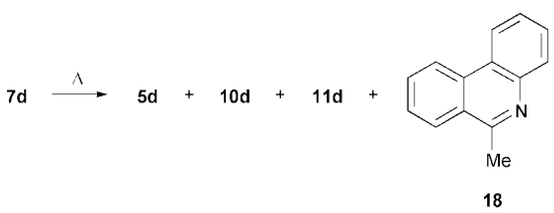
However, we think that this mechanism can be rejected for the following reasons. Whereas on the one hand it is plausible to



Scheme 5

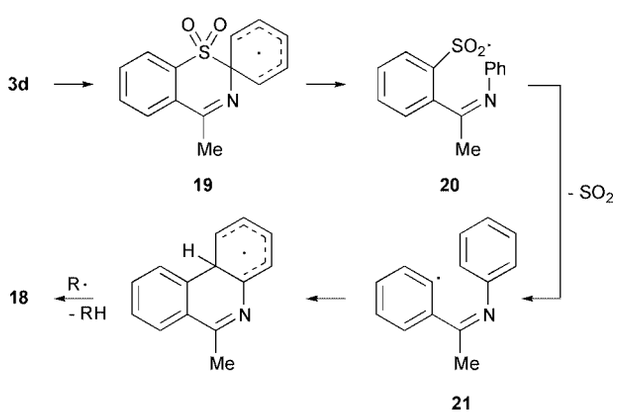
postulate a migration affording a stable thiophenoxyl radical, on the other hand it seems quite unreasonable that such a stable species could cyclise so efficiently as to give no traces of other compounds usually obtained from it (*e.g.*, disulfides).[13] In addition, although we did not succeed in generating thiophenoxyls **17** in solution by an independent route, it is worth pointing out that the accompanying FVP study on radicals **3** and **17**[8] confirmed that thiophenoxyls **17** can actually cyclise to give isothiazoles, but radicals **3** and **17** are definitely NOT interconverting species, contrary to what was observed with radicals **1**. This means that the formation of **14** from iminyls has to be explained by a direct S_Hi reaction of the iminyl radical onto the sulfur atom. This was confirmed for FVP conditions, but it can be stated with a reasonable degree of certainty that it is also the case for the solution conditions used in the present study.

When the sulfur atom is, in principle, no longer available for the S_Hi reaction, *i.e.* when it is oxidised to the sulfonyl group of radical **3d**, the homolytic aromatic substitution can actually occur instead of substitution at sulfur, although with low yields. Thus, decomposition of perester **7d** afforded, besides the usual compounds **4d**, **10d**, and **11d**, 6-methylphenanthridine **18** (10%) (Scheme 6).



Scheme 6

Formation of compound **18** can be rationalised through 1,6-spirocyclisation of iminyl **3d** to give spirocyclohexadienyl radical **19**, followed by 1,5-migration of the phenyl ring from sulfur to nitrogen to afford intermediate **20** (Scheme 7). Straightforward loss of sulfur dioxide from **20** affords the aryl radical **21**, which – due to the nature of the migration process – has the correct *Z*-geometry of the C–N double bond to allow cyclisation onto the *N*-phenyl ring to give **18**.



Scheme 7

Since iminyl radicals have a somewhat nucleophilic character[5j] – despite their moderately efficient addition to olefinic moieties – it is likely that the small amount of 1,6-ring closure observed with radical **3d** but not with **3a**–**c** could be due to the presence of the electron-withdrawing sulfonyl group, although spirocyclisation does not occur at one of the most electrophilic aromatic carbons. Radical migrations of aryl rings are in general rather uncommon, particularly when involving heteroatoms.[14] To our knowledge, the phenyl translocation observed in radical **3d** is the first example of homolytic 1,5-migration of an aryl ring from sulfur to nitrogen.

Conclusions

On the light of the above results, we can say that, like the corresponding aryloxy- and arylamino-substituted species, iminyl radicals **3a**–**d** are unable to give 7-membered cyclisation onto either the phenylsulfanyl or the phenylsulfonyl moieties. Iminyls **3a**–**c** afforded instead benzoisothiazole derivatives through 1,5-cyclisation onto the sulfur atom with concomitant release of a phenyl radical. It seems that closure of the 5-membered ring is a driving force strong enough to compensate for both elimination of a very reactive species and the formation of a rather weak sulfur–nitrogen bond. To our knowledge, this is the first example of S_Hi reaction of a nitrogen-centred radical onto a sulfide moiety.

On the other hand, iminyl radical **3d** gave 1,6-cyclisation to a small extent, resulting in the formation of a phenanthridine derivative. This arises from an unprecedented 1,5-aryl radical migration from the sulfur to the nitrogen atom, followed by loss of sulfur dioxide and cyclisation of an aryl radical. The different behaviour of radical **3d** could be the result of both the non-availability of the sulfur atom and the greater electrophilicity of the SO_2-phenyl ring, which would react faster with the slightly nucleophilic iminyl radical.

Experimental

General procedures

Mps were determined on an Electrothermal capillary apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded in deuteriochloroform on Varian Gemini 200 (200 MHz) or Gemini 300 (300 MHz) instruments, using tetramethylsilane as internal standard. Low- and high-resolution mass spectra were performed with a VG 7070E spectrometer by electron impact with a beam energy of 70 eV. IR spectra were recorded in chloroform solution on a Perkin-Elmer 257 spectrophotometer. Column chromatography was carried out on silica gel (ICN Silica, 63–200 mesh, 60 Å) or basic aluminium oxide (activity III, 70–230 mesh), using light petroleum (40–70 °C) and a light petroleum–diethyl ether gradient (from 0 up to 100% diethyl ether) as eluant. All the organic phases were dried over anhydrous sodium sulfate. Previously reported reaction products were identified by spectral comparison and mixed-mp determination with authentic specimens. When elemental analyses – or high resolution mass spectra – were not performed, the purity of the compounds was confirmed by the absence of any significant extraneous peak in the ^{1}H NMR spectra and/or by GC-MS analysis.

Starting materials

2-Chlorobenzaldehyde, 1-(2-chlorophenyl)ethanone, 2-chlorophenyl(phenyl)methanone, thiophenol, hydroxylamine hydrochloride, chloroacetic acid, CDI, and *tert*-butyl hydroperoxide (70 wt% in water) were commercially available (Aldrich); *tert*-butyl hydroperoxide was dried by extraction with cold light petroleum. 2-(Phenylsulfanyl)benzaldehyde[15] **4a**, 1-[2-(phenyl-

sulfanyl)phenyl]ethanone[16] **4b**, phenyl[2-(phenylsulfanyl)-phenyl]methanone[16] **4c**, phenyl[2-(phenylsulfanyl)phenyl]-methanone oxime[17] **5c**, and 6-methylphenanthridine[18] **18** were prepared according to the literature method.

1-[2-(Phenylsulfonyl)phenyl]ethanone 4d. In a round-bottomed, three-necked flask provided with mechanical stirring, condenser, and dropping funnel, ketone **4b** (9.0 g, 39.5 mmol) was solubilised in the minimum amount of glacial acetic acid. Hydrogen peroxide (30 wt% in water; 40 cm^3) was then added dropwise at rt to the stirred solution, and the resulting mixture was refluxed for 1 h. After cooling, the solvent was partly evaporated off and the residue was poured into ice–water and extracted with diethyl ether. The organic phase was washed with aqueous sodium hydrogen carbonate (5 wt%) and then dried; the solvent was finally evaporated to give the title compound **4d** (9.6 g, 93%) as an oil that slowly crystallised, mp 47–49 °C (Found: C, 64.2; H, 4.6. $C_{14}H_{12}O_3S$ requires C, 64.6; H, 4.6%); ν_{max}/cm^{-1} 1700, 1360 and 1150; δ_H (200 MHz) 2.70 (3 H, s, Me), 7.25–7.32 (1 H, m, Ar-H), 7.45–7.66 (5 H, m, Ar-H), 7.89–7.97 (2 H, m, Ar-H) and 8.00–8.08 (1 H, m, Ar-H); δ_C (50 MHz) 32.42, 126.53, 128.49, 129.58, 130.38, 130.49, 133.88, 138.54 (q), 141.85 (q), 142.90 (q) and 203.66 (q) (two C–H signals overlapped); *m/z* 245 ($M^+ - 15$, 100%), 217 (12), 195 (8), 181 (15), 167 (100), 153 (50), 105 (8) and 77 (36).

General procedure for the synthesis of the oximes 5a–d

According to a standard procedure,[19] a solution of the carbonyl compound and hydroxylamine hydrochloride (same amount in weight as the former) in a 10 : 1 v/v mixture of ethanol and pyridine (with the latter in same amount in volume as the carbonyl compound) was refluxed under mechanical stirring for one hour. Most of the solvent was evaporated off and the resulting mixture was poured into ice–water and extracted with diethyl ether. The organic phase was dried, the solvent was removed, and the residue recrystallised from light petroleum–benzene mixtures.

2-(Phenylsulfanyl)benzaldehyde oxime 5a. 4a (12.0 g, 56 mmol) gave oxime **5a** (11.0 g, 86%), mp 76–77 °C (Found: C, 68.5; H, 4.8; N, 6.0. $C_{13}H_{11}NOS$ requires C, 68.1; H, 4.8; N, 6.0%); ν_{max}/cm^{-1} 3580, 3330 and 1590; δ_H (200 MHz) 7.20–7.45 (8 H, m, Ar-H), 7.80–7.90 (1 H, m, Ar-H), 8.75 (1 H, s, CH=N) and 9.30 (1 H, s, OH); *m/z* 229.0570 (M^+, 42%. $C_{13}H_{11}NOS$ requires *M*, 229.0561), 212 (100), 197 (8), 184 (16), 134 (10), 109 (29), 77 (29) and 51 (21).

1-[2-(Phenylsulfanyl)phenyl]ethanone oxime 5b. 4b (15.0 g, 65.8 mmol) yielded oxime **5b** (15.2 g, 95%) as a 4 : 1 *E*/*Z* mixture (Found: C, 69.4; H, 5.4; N, 5.75. $C_{14}H_{13}NOS$ requires C, 69.1; H, 5.4; N, 5.8%); ν_{max}/cm^{-1} 3580, 3300, 3000, 1580, 1470, 1430, 1340 and 1010; *m/z* 243.0722 (M^+, 18%. $C_{14}H_{13}NOS$ requires *M*, 243.0718), 226 (100), 184 (17), 77 (14) and 51 (12). *E*-Isomer: mp 73–75 °C; δ_H (300 MHz) 2.28 (3 H, s, Me), 7.17–7.40 (9 H, m, Ar-H) and 8.14 (1 H, s, OH); the *E*-structure was confirmed by a NOE experiment in which irradiation of the OH signal caused a strong enhancement of the methyl singlet. *Z*-Isomer: mp 98–100 °C; δ_H (300 MHz) 2.17 (3 H, s, Me), 7.12–7.39 (9 H, m, Ar-H) and 8.13 (1 H, s, OH).

1-[2-(Phenylsulfonyl)phenyl]ethanone oxime 5d. For oxime **5d** the standard procedure was slightly modified as follows. A mixture of **4d** (15.5 g, 59.5 mmol), hydroxylamine hydrochloride (13.6 g, 197 mmol), ethanol (200 cm^3) and pyridine (50 cm^3, *i.e.* a threefold excess with respect to the standard quantity) was refluxed under mechanical stirring for 3 h. After standard work-up, the residue was chromatographed on silica gel (light petroleum–diethyl ether 80 : 20 as eluant) to give oxime **5d** (14.5 g, 89%) as a white solid, mp 130–132 °C (Found: C, 61.3; H, 4.7; N, 5.1. $C_{14}H_{13}NO_3S$ requires C, 61.1; H, 4.75; N, 5.1%); ν_{max}/cm^{-1} 3580, 3300, 1300 and 1150; δ_H (200 MHz) 2.15 (3 H, s, Me), 7.26–7.29 (1 H, m, Ar-H), 7.45–7.64 (5 H, m, Ar-H), 7.85–7.91 (2 H, m, Ar-H), 8.15–8.19 (1 H, m, Ar-H) and 8.86 (1 H, s, OH); signals ascribable to a second geometric isomer were also detected (trace amounts): 2.33 (s), 7.12–7.15 (m) and 7.34–7.45 (m); *m/z* 258 ($M^+ - 17$, 18%), 210 (89), 194 (100), 179 (23), 77 (41) and 51 (28).

General procedure for the synthesis of the iminoxyacetic acids 6a–d

According to the reported procedure,[3b] a mixture of oxime (30 mmol), chloroacetic acid (1.6 equiv.) and sodium hydroxide (3 equiv.) in water (25 cm^3)–ethanol (13 cm^3) was refluxed for several hours. Then it was poured into ice–water and neutralised with conc. hydrochloric acid. The mixture was extracted with dichloromethane, the organic phase was dried, the solvent removed, and the residue chromatographed.

[({[2-(Phenylsulfanyl)phenyl]methylidene}amino)oxy]acetic acid 6a. After 16 h, **5a** (11.0 g, 48.2 mmol) gave acid **6a** (8.6 g, 62%), mp 97–99 °C (from light petroleum–benzene) (Found: C, 63.0; H, 4.6; N, 5.0. $C_{15}H_{13}NO_3S$ requires C, 62.7; H, 4.6; N, 4.9%); ν_{max}/cm^{-1} 1740, 1590 and 1430; δ_H (200 MHz) 4.75 (2 H, s, CH_2), 7.15–7.40 (8 H, m, Ar-H), 7.82–7.90 (1 H, m, Ar-H) and 8.77 (1 H, s, N=CH); *m/z* 287.0621 (M^+, 13%. $C_{15}H_{13}NO_3S$ requires *M*, 287.0616), 212 (100), 211 (53), 210 (20), 184 (22), 136 (20), 109 (30) and 77 (30).

[({1-[2-(Phenylsulfanyl)phenyl]ethylidene}amino)oxy]acetic acid 6b. After 8 h, **5b** (16.1 g, 66.4 mmol) gave acid **6b** (13.0 g, 65%) as an oily 4 : 1 mixture of geometric isomers (Found: C, 64.2; H, 5.05; N, 4.6. $C_{16}H_{15}NO_3S$ requires C, 63.8; H, 5.0; N, 4.6%); ν_{max}/cm^{-1} 3500, 3060, 3000, 2940, 1770, 1735, 1585, 1110 and 1080; δ_H (200 MHz) 2.16 (0.2 × 3 H, s, Me, minor isomer), 2.31 (0.8 × 3 H, s, Me, major isomer), 4.48 (0.2 × 2 H, s, CH_2, minor isomer), 4.70 (0.8 × 2 H, s, CH_2, major isomer), 7.14–7.40 (9 H, m, Ar-H) and 10.56 (1 H, br s, OH); *m/z* 301.0770 (M^+, 11%. $C_{16}H_{15}NO_3S$ requires *M*, 301.0773), 226 (100), 184 (19), 150 (68), 109 (13), 77 (16) and 51 (13).

[({Phenyl[2-(phenylsulfanyl)phenyl]methylidene}amino)oxy]-acetic acid 6c. After 30 h, **5c** (17.6 g, 57.7 mmol) gave acid **6c** (11.5 g, 55%) as an oily 50 : 1 mixture of geometric isomers (Found: C, 69.8; H, 4.75; N, 3.85. $C_{21}H_{17}NO_3S$ requires C, 69.4; H, 4.7; N, 3.85%); ν_{max}/cm^{-1} 3500 vbr, 3050, 1780 and 1740; δ_H (200 MHz) 4.73 (0.98 × 1 H, br s, CH_2, major isomer), 4.75 (0.98 × 1 H, br s, CH_2, major isomer),[20] 4.84 (0.02 × 2 H, br s, CH_2, minor isomer), 7.24–7.47 (12 H, m, Ar-H), 7.50–7.59 (2 H, m, Ar-H) and 9.72 (1 H, br s, OH); *m/z* 363.0935 (M^+, 6%. $C_{21}H_{17}NO_3S$ requires *M*, 363.0929), 288 (100), 212 (60), 184 (28), 109 (16) and 77 (48).

[({1-[2-(Phenylsulfonyl)phenyl]ethylidene}amino)oxy]acetic acid 6d. After 4 h, **5d** (14.5 g, 52.8 mmol) gave acid **6d** (9.7 g, 55%) as a 6 : 1 mixture of geometric isomers, mp 107–109 °C (Found: C, 57.8; H, 4.55; N, 4.2. $C_{16}H_{15}NO_5S$ requires C, 57.6; H, 4.5; N, 4.2%); ν_{max}/cm^{-1} 3500, 3050, 1770, 1740, 1320 and 1160; δ_H (300 MHz) 2.10 (0.14 × 3 H, s, Me, minor isomer), 2.30 (0.86 × 3 H, s, Me, major isomer), 4.25 (0.14 × 2 H, AB system, *J* 16.7, CH_2, minor isomer),[20] 4.55 (0.86 × 2 H, s, CH_2, major isomer), 7.17–7.21 (0.14 × 1 H, m, Ar-H, minor isomer), 7.28–7.32 (0.86 × 1 H, m, Ar-H, major isomer), 7.43–7.69 (5 H, m, Ar-H), 7.85–7.92 (2 H, m, Ar-H), 8.09–8.13 (0.14 × 1 H, m, Ar-H, minor isomer) and 8.14–8.18 (0.86 × 1 H, dd, J_1 7.6, J_2 1.6, Ar-H, major isomer); *m/z* 258 ($M^+ - 75$, 6%), 194 (100), 152 (9), 77 (22) and 51 (16).

General procedure for the synthesis of the iminoxyperacetates 7a–d

According to the reported procedure,[21] the iminoxyacetic acid (10 mmol) was added at rt and under nitrogen to a stirred solution of CDI (1 equiv.) in anhydrous THF (15 cm^3). After 1 h, a solution of *tert*-butyl hydroperoxide (2.2 equiv.) in light petroleum (30 cm^3) was added dropwise at 0 °C and the mixture was kept at 0–5 °C for 4 h. The mixture was poured into ice–water and extracted with cold diethyl ether. The organic phase was washed twice with cold water and dried. After removal of the solvent the residue was chromatographed. Owing to the absence of molecular ions and decomposition hazard, neither high-resolution mass spectra nor elemental analyses were obtained for the peresters **7a**–**d**; their purity was, however, confirmed by the complete absence of any significant extraneous peak in their ^{1}H NMR spectra.

CAUTION. Since hydroperoxides and peresters are potentially hazardous compounds, they must be handled with due care; avoid exposure to strong heat or light, mechanical shock, oxidisable organic materials, or transition metal ions. No particular difficulties were experienced in handling any of the new peresters synthesised in this work using the procedure described above. Their column chromatography did not give any problem, even on a 10 g-scale; however, we advise performing the separation with extreme care, evaporating the solvent under reduced pressure with a water bath kept below 20 °C.

***tert*-Butyl [({[2-(phenylsulfanyl)phenyl]methylidene}amino)oxy]peracetate 7a.** Starting from **6a** (6.5 g, 22.7 mmol), perester **7a** was obtained (6.5 g, 80%) as an oil; δ_H (200 MHz) 1.20 (9 H, s, *tert*-Bu), 4.65 (2 H, s, CH_2), 7.05–7.30 (8 H, m, Ar-H), 7.75–7.80 (1 H, m, Ar-H) and 8.65 (1 H, s, N=CH); *m*/*z* 315 ($M^+ - 44$, 10%), 285 (15), 229 (17), 212 (97), 197 (13), 184 (23), 136 (15), 109 (17), 77 (23), 57 (100) and 51 (21).

***tert*-Butyl [({1-[2-(phenylsulfanyl)phenyl]ethylidene}amino)oxy]peracetate 7b.** Starting from **6b** (13.0 g, 43.2 mmol), perester **7b** was obtained (13.7 g, 85%) as an oily 6 : 1 mixture of geometric isomers; ν_{max}/cm^{-1} 2980, 1780, 1590, 1370, 1100 and 1000; δ_H (200 MHz) 1.30 (0.86 × 9 H, s, *tert*-Bu, major isomer), 1.33 (0.14 × 9 H, s, *tert*-Bu, minor isomer), 2.17 (0.14 × 3 H, s, Me, minor isomer), 2.30 (0.86 × 3 H, s, Me, major isomer), 4.49 (0.14 × 2 H, s, CH_2, minor isomer), 4.78 (0.86 × 2 H, s, CH_2, major isomer) and 7.38–7.72 (9 H, m, Ar-H); *m*/*z* 329 ($M^+ - 44$, 7%), 299 (6), 243 (7), 226 (100), 211 (7), 184 (15), 77 (11) and 57 (76).

***tert*-Butyl [({phenyl[2-(phenylsulfanyl)phenyl]methylidene}amino)oxy]peracetate 7c.** Starting from **6c** (7.77 g, 21.4 mmol), perester **7c** was obtained (8.0 g, 86%) as an oily 10 : 1 mixture of geometric isomers; δ_H (200 MHz) 1.30 (0.91 × 9 H, s, *tert*-Bu, major isomer), 1.33 (0.09 × 9 H, s, *tert*-Bu, minor isomer), 4.62 (0.91 × 1 H, br s, CH_2, major isomer), 4.67 (0.91 × 1 H, br s, CH_2, major isomer),[20] 4.80 (0.09 × 2 H, s, CH_2, minor isomer), 7.17–7.39 (12 H, m, Ar-H, both isomers), 7.45–7.52 (0.91 × 2 H, m, Ar-H, major isomer) and 7.56–7.62 (0.09 × 2 H, m, Ar-H, minor isomer); *m*/*z* 391 ($M^+ - 44$, 4%), 361 (6), 305 (5), 288 (100), 212 (43), 184 (21), 109 (13), 77 (35) and 57 (70).

***tert*-Butyl [({1-[2-(phenylsulfonyl)phenyl]ethylidene}amino)oxy]peracetate 7d.** Starting from **6d** (7.6 g, 22.8 mmol), perester **7d** was obtained (5.5 g, 60%) as a yellow, oily 4.5 : 1 mixture of geometric isomers; this was the only perester that showed partial decompostition during chromatographic work-up; δ_H (200 MHz) 1.28 (0.18 × 9 H, s, *tert*-Bu, minor isomer), 1.30 (0.82 × 9 H, s, *tert*-Bu, major isomer), 2.30 (0.82 × 3 H, s, Me, major isomer), 2.69 (0.18 × 3 H, s, Me, minor isomer), 4.00 (0.18 × 2 H, AB system, *J* 15.9, CH_2, minor isomer),[20] 4.55 (0.82 × 2 H, s, CH_2, major isomer), 7.19–7.64 (6 H, m, Ar-H, both isomers), 7.82–7.96 (2 H, m, Ar-H, both isomers), 8.01–8.07 (0.18 × 1 H, m, Ar-H, minor isomer) and 8.13–8.22 (0.82 × 1 H, m, Ar-H, major isomer); *m*/*z* 331 ($M^+ - 74$, 6%), 275 (42), 258 (73), 210 (98), 194 (100), 179 (43), 167 (24), 77 (42) and 57 (79).

General procedure for the decomposition of peresters 7a–d

A bromobenzene (50 cm^3) solution of the perester (10 mmol) was added dropwise in 1 h to 450 cm^3 of boiling bromobenzene. After one additional hour at reflux, the solution was cooled, the solvent was evaporated off, and the residue chromatographed.

From 7a. Perester **7a** (15 mmol) gave, in order of elution, *2-(phenylsulfanyl)benzaldehyde O-(tert-butyl)oxime* **11a** (0.26 g, 6%) as an oily 6 : 1 mixture of geometric isomers; δ_H (200 MHz) 1.32 (0.14 × 9 H, s, *tert*-Bu, minor isomer), 1.35 (0.86 × 9 H, s, *tert*-Bu, major isomer), 7.10–7.60 (9 H, m, Ar-H), 8.57 (0.86 × 1 H, s, N=CH, major isomer) and 8.62 (0.14 × 1 H, s, N=CH, minor isomer); *m*/*z* 285.1189 (M^+, 9%. $C_{17}H_{19}NOS$ requires *M*, 285.1187), 229 (10), 212 (77), 184 (23), 109 (16), 77 (25) and 57 (100); *2-(phenylsulfanyl)benzaldehyde O-(tert-butoxymethyl)oxime* **10a** (0.85 g, 18%) as an oily 17 : 1 mixture of geometric isomers; δ_H (200 MHz) 1.28 (9 H, s, *tert*-Bu), 5.35 (0.05 × 2 H, s, CH_2, minor isomer), 5.40 (0.95 × 2 H, s, CH_2, major isomer), 7.10–8.10 (9 H, m, Ar-H) and 8.70 (1 H, s, N=CH); *m*/*z* 315.1298 (M^+, 3%. $C_{18}H_{21}NO_2S$ requires *M*, 315.1293), 285 (5), 229 (10), 212 (50), 211 (100), 210 (55), 184 (50), 109 (18), 77 (35) and 57 (68); aldehyde **4a** (0.90 g, 28%); *2-(phenylsulfanyl)benzonitrile* **12a** (0.16 g, 5%), mp 34–36 °C [lit.,[22] 35–37 °C, NMR data non-reported]; ν_{max}/cm^{-1} 2220; δ_H (200 MHz) 7.05–7.11 (1 H, m, Ar-H), 7.16–7.25 (2 H, m, Ar-H), 7.30–7.47 (5 H, m, Ar-H) and 7.56–7.62 (1 H, m, Ar-H); *m*/*z* 211 (M^+, 100%), 210 (34), 184 (41), 109 (11), 77 (43) and 51 (87) [lit.,[22] 211 (M^+, 100%), 109 (60) and 51 (42)].

From 7b. Perester **7b** (15 mmol) gave, in order of elution, a mixture of *o*-, *m*- and *p*-bromobiphenyl (0.65 g, 19% overall yield) in the proportions 50 : 35 : 15 [lit.,[12] proportions for radical phenylation of bromobenzene are 49.3 : 33.3 : 17.4]; *1-[2-(phenylsulfanyl)phenyl]ethanone O-(tert-butyl)oxime* **11b** (0.31 g, 7%) as an oily 5 : 1 mixture of geometric isomers; δ_H (200 MHz) 1.20 (0.83 × 9 H, s, *tert*-Bu, major isomer), 1.34 (0.17 × 9 H, s, *tert*-Bu, minor isomer), 2.17 (0.83 × 3 H, s, Me, major isomer), 2.23 (0.17 × 3 H, s, Me, minor isomer) and 7.01–8.01 (9 H, m, Ar-H); *m*/*z* 299.1341 (M^+, 6%. $C_{18}H_{21}NOS$ requires *M*, 299.1344), 226 (100), 184 (14), 77 (10) and 57 (50); *3-methyl-1,2-benzoisothiazole* **14b** (0.4 g, 18%), oil; hydrochloride, mp 108–110 °C [lit.,[23] 116 °C]; δ_H (200 MHz) 2.70 (3 H, s, Me), 7.31–7.49 (2 H, m, Ar-H), 7.81–7.88 (2 H, m, Ar-H) [lit.,[24] 2.75 (3 H, s), 7.42 (2 H, m) and 7.92 (2 H, m)]; δ_C (50 MHz) 17.38, 119.79, 123.35, 124.45, 127.46, 135.01, 152.00 and 162.79 [lit.,[24] δ_C 17.39, 119.49, 123.36, 124.44, 127.43, 135.03, 152.03 and 162.80]; *m*/*z* 149.0300 (M^+, 100%. C_8H_7NS requires *M*, 149.0299), 148 (52), 121 (50) and 108 (30); *1-[2-(phenylsulfanyl)phenyl]ethanone O-(tert-butoxymethyl)oxime* **10b** (0.63 g, 13%) as an oily 2.4 : 1 mixture of geometric isomers; ν_{max}/cm^{-1} 2980, 1580, 1470, 1430, 1370, 1090 and 980; δ_H (200 MHz) 1.13 (0.29 × 9 H, s, *tert*-Bu, minor isomer), 1.25 (0.71 × 9 H, s, *tert*-Bu, major isomer), 2.17 (0.29 × 3 H, s, Me, minor isomer), 2.22 (0.71 × 3 H, s, Me, major isomer), 5.08 (0.29 × 2 H, s, CH_2, minor isomer), 5.32 (0.71 × 2 H, s, CH_2, major isomer) and 7.25–7.38 (9 H, m, Ar-H, both isomers); *m*/*z* 329.1456 (M^+, 12%. $C_{19}H_{23}NO_2S$ requires *M*, 329.1450), 243 (10), 228 (34), 226 (72), 213 (57), 184 (24), 77 (21) and 57 (100); ketone **4b** (0.56 g, 16%); oxime **5b** (0.35 g, 10%).

From 7c. Perester **7c** (15 mmol) gave, in order of elution, a mixture of *o*-, *m*- and *p*-bromobiphenyl (0.97 g, 28% overall yield) in the proportions 47 : 33 : 20 [lit.,[12] proportions for

radical phenylation of bromobenzene are 49.3 : 33.3 : 17.4]; presumably *phenyl[2-(phenylsulfanyl)phenyl]methanone O-(tert-butyl)oxime* **11c** (trace amounts), *m/z* 361.1506 (M^+, 5%. $C_{23}H_{23}NOS$ requires *M*, 361.1500), 288 (100), 184 (23), 77 (25) and 57 (60); *phenyl[2-(phenylsulfanyl)phenyl]methanone O-(tert-butoxymethyl)oxime* **10c** (1.37 g, 24%) as an oily 8.4 : 1 mixture of geometric isomers partially separated by column chromatography; δ_H (200 MHz, major isomer) 1.20 (9 H, s, *tert*-Bu), 5.24 (1 H, br s, CH_2), 5.33 (1 H, br s, CH_2),[20] 7.16–7.35 (12 H, m, Ar-H) and 7.51–7.57 (2 H, m, Ar-H); δ_H (200 MHz, minor isomer) 1.25 (9 H, s, *tert*-Bu), 5.37 (2 H, s, CH_2), 7.10–7.40 (12 H, m, Ar-H) and 7.77–7.83 (2 H, m, Ar-H); *m/z* (both isomers) 391 (M^+, <1%), 361 (<1), 305 (4), 288 (100), 212 (23), 184 (23), 109 (8), 77 (25) and 57 (86); *3-phenyl-1,2-benzoisothiazole* **14c** (0.8 g, 25%), mp 68–69 °C [lit.,[25] 71 °C]; δ_H (200 MHz) 7.42–7.62 (5 H, m, Ar-H), 7.85–7.92 (2 H, m, Ar-H), 7.97–8.03 (1 H, m, Ar-H) and 8.17–8.23 (1 H, m, Ar-H) [lit.,[25] 7.40–8.35]; *m/z* 211.0460 (M^+, 100%. $C_{13}H_9NS$ requires *M*, 211.0456), 210 (75), 184 (14), 108 (13) and 77 (33); *phenyl[2-(phenylsulfanyl)phenyl]methanimine* **13c** (0.68 g, 16%); ν_{max}/cm^{-1} 3280, 1610, 1590 and 1580; δ_H (200 MHz) 7.26–7.48 (12 H, m, Ar-H) and 7.61–7.71 (2 H, m, Ar-H) (N-H non-visible); *m/z* 289.0920 (M^+, 21%. $C_{19}H_{15}NS$ requires *M*, 289.0925), 288 (6), 212 (100), 184 (8), 109 (21) and 77 (36); ketone **4c** (0.47 g, 11%); oxime **5c** (0.18 g, 4%).

From 7d. Perester **7d** (8 mmol) gave, in order of elution, *1-[2-(phenylsulfonyl)phenyl]ethanone O-(tert-butyl)oxime* **11d** (0.1 g, 4%), as an oily 4 : 1 mixture of geometric isomers; δ_H (200 MHz) 1.00 (0.2 × 9 H, s, *tert*-Bu, minor isomer), 1.25 (0.8 × 9 H, s, *tert*-Bu, major isomer), 2.20 (0.8 × 3 H, s, Me, major isomer), 2.30 (0.2 × 3 H, s, Me, minor isomer) and 7.05–8.15 (9 H, m, Ar-H); *m/z* 275 ($M^+ - 56$, 9%), 258 (50), 210 (100), 194 (85), 179 (45), 165 (16), 151 (28), 134 (15), 77 (36) and 57 (55); *6-methylphenanthridine* **18** (0.15 g, 10%), mp 81–82 °C [lit.,[18] 80–82 °C]; δ_H (200 MHz) 3.05 (3 H, s, Me), 7.59–7.77 (3 H, m, Ar-H), 7.87 (1 H, m, Ar-H), 8.13 (1 H, dd, J_1 8.0, J_2 1.4, Ar-H), 8.25 (1 H, dd, J_1 8.0, J_2 1.0, Ar-H), 8.57 (1 H, dd, J_1 7.0, J_2 1.0, Ar-H) and 8.66 (1 H, br d, *J* 7.5, Ar-H); [lit.,[26] (300 MHz) 3.06 (3 H, s), 7.62 (1 H, t, *J* 8.0), 7.69 (2 H, t, *J* 8.0), 7.84 (1 H, t, *J* 8.0), 8.08 (1 H, d, *J* 8.1), 8.22 (1 H, d, *J* 7.5), 8.54 (1 H, d, *J* 8.0) and 8.63 (1 H, d, *J* 8.3)]; *m/z* 193 (M^+, 100%), 192 (15), 178 (32), 165 (41), 151 (39) and 76 (20);[27] *1-[2-(phenylsulfonyl)-phenyl]ethanone O-(tert-butoxymethyl)oxime* **10d** (0.81 g, 28%) as an oily 13 : 1 mixture of geometric isomers partially separated by column chromatography; ν_{max}/cm^{-1} 2980, 2930, 1600, 1370, 1310 and 1150; δ_H (200 MHz, major isomer) 1.30 (9 H, s, *tert*-Bu), 2.30 (3 H, s, Me), 5.20 (2 H, s, CH_2), 7.23–7.30 (1 H, m, Ar-H), 7.41–7.62 (5 H, m, Ar-H), 7.97–8.03 (2 H, m, Ar-H) and 8.11–8.17 (1 H, m, Ar-H); δ_H (200 MHz, minor isomer) 1.00 (9 H, s, *tert*-Bu), 2.32 (3 H, s, Me), 4.45 (2 H, AB system, *J* 8.1, CH_2)[20] and 7.07–8.25 (9 H, m, Ar-H); *m/z* (both isomers) 275 ($M^+ - 86$, 18%), 258 (60), 210 (87), 194 (100), 179 (47), 134 (36), 77 (43) and 57 (80); ketone **4d** (0.33 g, 16%).

Acknowledgements

The authors gratefully acknowledge financial support from CNR (Rome), MURST (2000–2001 Grant for 'Radical Processes in Chemistry and Biology: Syntheses, Mechanisms, and Applications'), and the University of Bologna (1999–2001 Funds for Selected Research Topics).

References and notes

1 D. P. Curran, *Comprehensive Organic Synthesis*, ed. B. M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, vol. 4, p. 715; W. B. Motherwell and D. Crich, *Free Radical Chain Reactions in Organic Synthesis*, Academic Press, London, 1992; M. J. Perkins, *Radical Chemistry*, Ellis Horwood, London, 1994; D. P. Curran, N. A. Porter and B. Giese, *Stereochemistry of Radical Reactions*, VCH, Weinheim, 1996.

2 (*a*) M. L. Poutsma and P. A. Ibraria, *J. Org. Chem.*, 1969, **34**, 2848; (*b*) M. C. R. Symons, *Tetrahedron*, 1973, **29**, 615; (*c*) D. Griller, G. D. Mendenhall, W. Van Hoof and K. U. Ingold, *J. Am. Chem. Soc.*, 1974, **96**, 6068; (*d*) B. P. Roberts and J. Winter, *J. Chem. Soc., Perkin Trans. 2*, 1979, 1353.

3 (*a*) A. R. Forrester, M. Gill, C. J. Meyer, J. S. Sadd and R. H. Thomson, *J. Chem. Soc., Chem. Commun.*, 1975, 291; (*b*) A. R. Forrester, M. Gill, C. J. Meyer, J. S. Sadd and R. H. Thomson, *J. Chem. Soc., Perkin Trans. 1*, 1979, 606; (*c*) A. R. Forrester, M. Gill, J. S. Sadd and R. H. Thomson, *J. Chem. Soc., Perkin Trans. 1*, 1979, 612; (*d*) A. R. Forrester, M. Gill and R. H. Thomson, *J. Chem. Soc., Perkin Trans. 1*, 1979, 616, 621; (*e*) A. R. Forrester, M. Gill, R. Napier and R. H. Thomson, *J. Chem. Soc., Perkin Trans. 1*, 1979, 632; (*f*) A. R. Forrester, M. Gill, C. J. Meyer and R. H. Thomson, *J. Chem. Soc., Perkin Trans. 1*, 1979, 637; (*g*) A. R. Forrester, R. Napier and R. H. Thomson, *J. Chem. Soc., Perkin Trans. 1*, 1981, 984; (*h*) A. R. Forrester, H. Irikawa, R. H. Thomson and S.-O. Woo, *J. Chem. Soc., Perkin Trans. 1*, 1981, 1712; (*i*) S. Atmaram, A. R. Forrester, M. Gill and R. H. Thomson, *J. Chem. Soc., Perkin Trans. 1*, 1981, 1721.

4 (*a*) W. D. Crow, H. McNab and J. M. Philip, *Aust. J. Chem.*, 1976, **29**, 2299; (*b*) H. McNab, *J. Chem. Soc., Chem. Commun.*, 1980, 422; (*c*) H. McNab, *J. Chem. Soc., Perkin Trans. 1*, 1982, 1941; (*d*) H. McNab, *J. Chem. Soc., Perkin Trans. 1*, 1984, 371; (*e*) H. McNab, *J. Chem. Soc., Perkin Trans. 1*, 1984, 377; (*f*) H. McNab and G. S. Smith, *J. Chem. Soc., Perkin Trans. 1*, 1984, 381; (*g*) C. L. Hickson and H. McNab, *J. Chem. Soc., Perkin Trans. 1*, 1984, 1569.

5 (*a*) J. Boivin, E. Fouquet and S. Z. Zard, *Tetrahedron Lett.*, 1990, **31**, 85, 3545; (*b*) J. Boivin, E. Fouquet and S. Z. Zard, *J. Am. Chem. Soc.*, 1991, **113**, 1054; (*c*) J. Boivin, E. Fouquet and S. Z. Zard, *Tetrahedron Lett.*, 1991, **32**, 4299; (*d*) J. Boivin, A.-M. Schiano and S. Z. Zard, *Tetrahedron Lett.*, 1992, **33**, 7849; (*e*) J. Boivin, E. Fouquet and S. Z. Zard, *Tetrahedron*, 1994, **50**, 1745, 1757, 1769; (*f*) J. Boivin, A.-M. Schiano and S. Z. Zard, *Tetrahedron Lett.*, 1994, **35**, 249; (*g*) A.-C. Callier-Dublanchet, B. Quiclet-Sire and S. Z. Zard, *Tetrahedron Lett.*, 1995, **36**, 8791; (*h*) J. Boivin, A.-C. Callier-Dublanchet, B. Quiclet-Sire, A.-M. Schiano and S. Z. Zard, *Tetrahedron*, 1995, **51**, 6517; (*i*) S. Z. Zard, *Synlett*, 1996, 1148; (*j*) M.-H. Le Tadic-Biadatti, A.-C. Callier-Dublanchet, J. H. Horner, B. Quiclet-Sire, S. Z. Zard and M. Newcomb, *J. Org. Chem.*, 1997, **62**, 559; (*k*) A.-C. Callier-Dublanchet, B. Quiclet-Sire and S. Z. Zard, *Tetrahedron Lett.*, 1997, **38**, 2463; (*l*) F. Gagosz and S. Z. Zard, *Synlett*, 1999, 1978; (*m*) J. Boivin, A.-M. Schiano, S. Z. Zard and H. Zhang, *Tetrahedron Lett.*, 1999, **40**, 4531.

6 For other studies on iminyl radicals see also (*a*) H. Sakuragi, S.-I. Ishikawa, T. Nishimura, M. Yoshida, N. Inamoto and K. Tokumaru, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 1949; (*b*) R. F. Hudson and K. A. F. Record, *J. Chem. Soc., Chem. Commun.*, 1976, 539; (*c*) D. L. J. Clive, P. L. Beaulieu and L. Set, *J. Org. Chem.*, 1984, **49**, 1313; (*d*) M. Hasebe, K. Kogawa and T. Tsuchiya, *Tetrahedron Lett.*, 1984, **25**, 3887; (*e*) B. Chenera, C. P. Chuang, D. J. Hart and L. Y. Hsu, *J. Org. Chem.*, 1985, **50**, 5409; (*f*) R. Tsang and B. Fraser-Reid, *J. Am. Chem. Soc.*, 1986, **108**, 2116; (*g*) A. L. J. Beckwith, D. M. O'Shea, S. Gerba and S. W. Westwood, *J. Chem. Soc., Chem. Commun.*, 1987, 666; (*h*) A. L. J. Beckwith, D. M. O'Shea and S. W. Westwood, *J. Am. Chem. Soc.*, 1988, **110**, 2565; (*i*) B. W. Yeung, J. L. M. Contelles and B. Fraser-Reid, *J. Chem. Soc., Chem. Commun.*, 1989, 1160; (*j*) J. K. Dickson, Jr., R. Tsang, J. M. Llera and B. Fraser-Reid, *J. Org. Chem.*, 1989, **54**, 5350; (*k*) S. Knapp, F. S. Gibson and Y. H. Choe, *Tetrahedron Lett.*, 1990, **31**, 5397; (*l*) B. B. Snider and B. O. Buckman, *J. Org. Chem.*, 1992, **57**, 322; (*m*) C.-C. Yang, H.-T. Chang and J.-M. Fang, *J. Org. Chem.*, 1993, **58**, 3100; (*n*) L. Elkaim and C. Meyer, *J. Org. Chem.*, 1996, **61**, 1556; (*o*) V. Sridar and G. Babu, *Synth. Commun.*, 1997, **27**, 323; (*p*) E. G. Janzen and D. E. Nutter, *Magn. Reson. Chem.*, 1997, **35**, 131; (*q*) P. C. Montevecchi, M. L. Navacchia and P. Spagnolo, *J. Org. Chem.*, 1997, **62**, 5846; (*r*) R. Leardini, D. Nanni, P. Pareschi, A. Tundo and G. Zanardi, *J. Org. Chem.*, 1997, **62**, 8394; (*s*) R. Leardini, D. Nanni, A. Tundo and G. Zanardi, *Tetrahedron Lett.*, 1998, **39**, 2441; (*t*) C. M. Camaggi, R. Leardini, D. Nanni and G. Zanardi, *Tetrahedron*, 1998, **54**, 5587; (*u*) G. A. Russell and P. Chen, *J. Phys. Org. Chem.*, 1998, **11**, 715; (*v*) X. Lin, D. Stien and S. M. Weinreb, *Org. Lett.*, 1999, **1**, 637; (*w*) M. Depature, J. Diewok, J. Grimaldi and J. Hatem, *Eur. J. Org. Chem.*, 2000, 275. See also: A. G. Fallis and I. M. Brinza, *Tetrahedron*, 1997, **53**, 17543 for an extensive review on iminyls and other nitrogen-centred radicals.

7 (*a*) G. Calestani, R. Leardini, H. McNab, D. Nanni and G. Zanardi, *J. Chem. Soc., Perkin Trans. 1*, 1998, 1813; (*b*) M. Black, J. I. G. Cadogan, R. Leardini, H. McNab, G. McDougald, D. Nanni,

D. Reed and A. Zompatori, *J. Chem. Soc.*, *Perkin Trans. 1*, 1998, 1825; (*c*) R. Leardini, H. McNab, D. Nanni, S. Parsons, D. Reed and A. G. Tenan, *J. Chem. Soc.*, *Perkin Trans. 1*, 1998, 1833.
8 For the results obtained in the gas phase we refer to our following paper: T. Creed, R. Leardini, H. McNab, D. Nanni, I. S. Nicolson and D. Reed, *J. Chem. Soc.*, *Perkin Trans. 1*, 2001, DOI 10.1039/b009844m, accompanying paper in this issue.
9 (*a*) S. Guidotti, R. Leardini, D. Nanni, P. Pareschi and G. Zanardi, *Tetrahedron Lett.*, 1995, **36**, 451; (*b*) R. Leardini, H. McNab and D. Nanni, *Tetrahedron*, 1995, **51**, 12143; (*c*) R. Leardini, D. Nanni, M. Santori and G. Zanardi, *Tetrahedron*, 1992, **48**, 3961.
10 L. Craine and M. Raban, *Chem. Rev.*, 1989, **89**, 689. Even aliphatic sulfenimides are sometimes difficult to obtain: see Ref. 6*o*.
11 Semiempirical calculations (MNDO-d) predict for benzothiazole a heat of formation about 25.1 kJ mol^{-1} lower than that of the benzoisothiazole **14a.**
12 D. H. Hey, *Adv. Free-Radical Chem.*, 1967, **2**, 47.
13 Thiophenoxyl dimers were detected even under FVP conditions (see accompanying paper) and are therefore to be expected with better reason in solution.
14 For radical translocations see: T. H. Lowry and K. S. Richardson, *Mechanism and Theory in Organic Chemistry*, Harper and Row, New York, 3rd edn., 1987, ch. 9, p. 800; D. C. Nonhebel and J. C. Walton, *Free-Radical Chemistry, Structure and Mechanism*, Cambridge University Press, Cambridge, 1974, ch. 13, p. 498; J. W. Wilt, *Free Radical Rearrangements* in *Free Radicals*, ed. J. K. Kochi, Wiley, New York, 1973, ch. 8, p. 333. For homolytic aryl migrations in the liquid phase see: R. Leardini, D. Nanni, G. F. Pedulli, A. Tundo and G. Zanardi, *J. Chem. Soc.*, *Perkin Trans. 1*, 1986, 1591; E. Lee, C. Lee, J. S. Tae, H. S. Whang and K. S. Li, *Tetrahedron Lett.*, 1993, **34**, 2343; W. B. Motherwell and A. M. K. Pennell, *J. Chem. Soc.*, *Chem. Commun.*, 1991, 877; L. Benati, L. Capella, P. C. Montevecchi and P. Spagnolo, *J. Org. Chem.*, 1994, **59**, 2818; L. Capella, P. C. Montevecchi and D. Nanni, *J. Org. Chem.*, 1994, **59**, 3368; R. Leardini, D. Nanni, G. F. Pedulli, A. Tundo, G. Zanardi, E. Foresti and P. Palmieri, *J. Am. Chem. Soc.*, 1989, **111**, 7723 and references cited therein; for homolytic aryl migrations in the gas phase see: Ref. 4*f*; J. I. G. Cadogan, H. S. Hutchison and H. McNab, *J. Chem. Soc.*, *Perkin Trans. 1*, 1987, 1407; M. Black, J. I. G. Cadogan and H. McNab, *J. Chem. Soc.*, *Chem. Commun.*, 1990, 395.
15 S. Ohno, H. Shimizu, T. Kataoka and M. Hori, *J. Org. Chem.*, 1984, **49**, 2472.
16 G. Capozzi, G. Melloni and G. Modena, *J. Chem. Soc.*, *Perkin Trans. 1*, 1973, 2250.
17 R. Leardini, L. Lunazzi, A. Mazzanti, H. McNab and D. Nanni, *Eur. J. Org. Chem.*, 2000, 3439.
18 S. V. Kessar, D. Pal and M. Singh, *Tetrahedron*, 1973, **29**, 177.
19 *Vogel's Textbook of Practical Organic Chemistry*, Longman, Harlow, 5th edn., 1989, p. 1259.
20 The diastereotopicity shown by the OCH_2 protons of the *Z*-isomers of *ortho*-substituted aryloxime derivatives has been recently discussed (see Ref. 17).
21 L. A. Singer and N. P. Kong, *J. Am. Chem. Soc.*, 1967, **89**, 5251; H. A. Staab, *Angew. Chem.*, *Int. Ed. Engl.*, 1962, **1**, 351.
22 J. V. Allen, S. J. Coote, G. J. Dawson, C. G. Frost, C. J. Martin and J. M. J. Williams, *J. Chem. Soc.*, *Perkin Trans. 1*, 1994, 2065.
23 R. J. Crawford and C. Woo, *J. Org. Chem.*, 1966, **31**, 1655.
24 S. L. Buchwald, B. T. Watson, R. T. Lum and W. A. Nugent, *J. Am. Chem. Soc.*, 1987, **109**, 7137.
25 D. M. McKinnon and K. D. Lee, *Can. J. Chem.*, 1988, **66**, 1405.
26 J. J. S. Lamba and J. M. Tour, *J. Am. Chem. Soc.*, 1994, **116**, 11723.
27 All of the compounds containing the SO_2 moiety (*e.g.*, **4d** and **5d**) were stable at the reaction temperature, *i.e.* no loss of sulfur dioxide was observed: therefore it can be reasonably inferred that loss of SO_2 to give the phenanthridine **18** must occur during a radical cyclisation pathway.