EPR studies of nitrogen-centred free radicals. Part 50.[1] Unusual decomposition behaviour of isolable stable thioaminyl free radicals at high temperature

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Thermal stabilities of *N*-(4-nitrophenylthio)-*N*-(4-*tert*-butyl-2,6-diphenylphenyl)aminyl 1a, *N*-(4-nitrophenylthio)-*N*-(2,4,6-triphenylphenyl)aminyl 2a, *N*-(2,4-dichlorophenylthio)-*N*-2,4,6-triphenylphenyl)aminyl 2b and *N*-(4-nitrophenylthio)-*N*-(2-*tert*-butyl-4,6-diphenylphenyl)aminyl 3a have been studied. When 1a, 2a and 2b are heated in degassed benzene at 80 °C for 24–30 h, they almost completely decompose, giving two non-radical compounds. On the other hand, 3a is thermally much more stable and the complete decomposition requires heating for 8 days. On the basis of the product analysis study the thermal decomposition mechanism is proposed and the reason why 3a is so stable at high temperature is discussed.

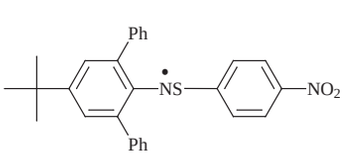
Introduction

Free radicals are inherently transient species because there is an electron vacancy in the highest occupied molecular orbital. However, electronic stabilization and steric protection would render them persistent. The most extreme examples are isolable stable free radicals represented by aminoxyl radicals, nitronyl aminoxyls, *N*,*N*-diphenyl-1-picrylhydrazyl (DPPH) and verdazyls,[2] *etc.* In recent years, isolable stable free radicals have attracted much attention in the studies on organic magnetism[3] and 'living' free radical polymerization.[4]

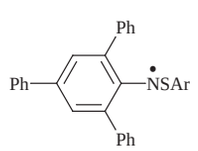
As part of the program toward organic magnetism,[5] we have searched for a new class of isolable free radicals. Thioaminyl radicals (ArṄSAr′), a new class of stable free radicals, are electronically stabilized by the conjugative delocalization of the unpaired electron from the nitrogen to the sulfur (Scheme 1).

Scheme 1

However, they are not so long-lived because irreversible homolytic reactions occurring at the anilino *ortho* and *para* positions destroy the radicals.[6,7] For example, PhṄSPh is decomposed *via* C–N coupling to give *p*-benzoquinone diimine in 40% yield as a main non-radical product.[8] Therefore, if the anilino benzene ring can be completely protected from such reactions, they may be isolable radicals. We have prepared a variety of sterically protected thioaminyls and found that *N*-(arylthio)-*N*-(4-*tert*-butyl-2,6-diphenylphenyl)aminyls **1**, *N*-(arylthio)-*N*-(2,4,6-triphenylphenyl)aminyls **2**, and *N*-(arylthio)-*N*-(2-*tert*-butyl-2,6-diphenylphenyl)aminyls **3** are isolable radicals.[9–11] Although these radicals persist for a long time in solution at room temperature without decomposition, slow decomposition occurs at high temperatures. For example, when **1** and **2** were heated in benzene at 80 °C for 24–30 h, they were almost completely decomposed to non-radical compounds. In contrast, aminyl **3** is much more stable than **1** and **2**, and the complete decomposition required heating for 8 days. To clarify their thermal decomposition mechanism and to elucidate the reason why only **3** is thermally much more stable, the product analyses for the decomposition were performed, and we have found that the first step of the decomposition is an intramolecular homolytic attack of the nitrogen radical centre to one of the *ortho* positions of the 2- and 6-phenyl group attached to the anilino group. To our knowledge, such a decomposition behaviour has not been found for isolable stable free radicals, and this is an important finding in the study of stable free radical chemistry. Herein we describe the thermal stabilities of **1**, **2** and **3**, the product analyses for the thermal decomposition and the thermal decomposition mechanism.



1a



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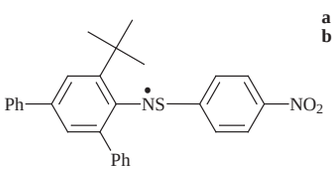
a Ar = 4-$NO_2C_6H_4$
b Ar = 2,4-$Cl_2C_6H_3$



3a

Results and discussion

The thermal decomposition for the isolable stable thioaminyl free radicals was carried out in oxygen-free benzene at 80 °C. The radicals used in this study are *N*-(4-nitrophenylthio)-*N*-(4-*tert*-butyl-2,6-diphenylphenyl)aminyls **1a**,[11] *N*-(4-nitrophenylthio)-*N*-(2,4,6-triphenylphenyl)aminyls **2a**,[9] *N*-(2,4-dichlorophenylthio)-*N*-(2,4,6-triphenylphenyl)aminyls **2b**[9] and *N*-(4-nitrophenylthio)-*N*-(2-*tert*-butyl-2,6-diphenylphenyl)aminyls **3a**,[11] which are more stable and easily obtained than the others. The reactions were carried out under oxygen-free conditions to avoid secondary reactions of the products with oxygen. Complete decomposition of the thioaminyl radicals was clearly indicated by disappearance of the characteristic colour of the radicals [**1a**, purple (583 and 492 nm); **2a**, yellowish green (637 and 513 nm); **2b**, bluish green (637 and 535 nm); **3a**, green (641 and 512 nm)]. When the characteristic colours almost disappeared (24 h–8 days), the reaction mixtures were inspected by TLC. Since column chromatographic separation of the products on silica gel or alumina caused complete decomposition of some products (**6** and **8**) during chromatography, the isolation was performed with a preparative GPC instrument. The structures of the products isolated were elucidated on the basis of IR,

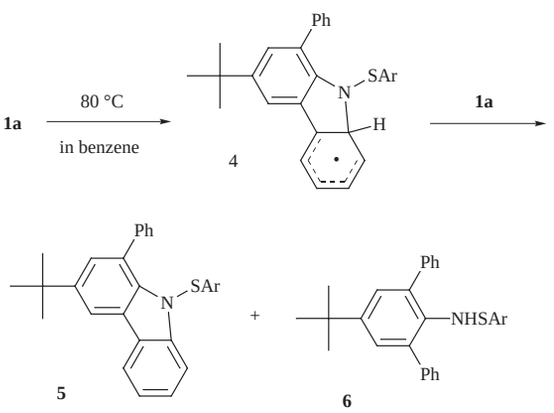
Table 1 Thermal decomposition of thioaminyl radicals in oxygen-free benzene at 80 °C

Entry	Radical	*t*/h [a]	Product (% yield) [b]
1	**1a**	24	**5** (50), **6** (43)
2	**2a**	28	**7a** (49), **8a** (48)
3	**2b**	30	**7b** (43), **8b** (48)
4	**3a**	192	**11** (48)

[a] The time required for the almost complete decomposition of radical. [b] Isolated yield.

^{1}H NMR and mass spectra. The results are summarized in Table 1.

When **1a** was heated in oxygen-free benzene for 24 h, it was almost completely decomposed. TLC analysis of the reaction mixture showed formation of two products (Scheme 2). One



Ar = 4-$NO_2C_6H_4$

Scheme 2

product (less mobile) was shown to be the known compound, **6**, by comparison of the IR and ^{1}H NMR spectra with those of the authentic sample. Compound **6** is the corresponding precursor of **1a**. The other, more mobile, product was an unknown compound, **5**. The IR spectra showed no absorption due to the NH stretching vibration around 3300 cm^{-1}. The mass spectrum gave a strong peak at *m*/*z* 452 as the molecular ion (M^+) which corresponds to **1a** − H, indicating that the product is formed by hydrogen-atom abstraction from **1a**. The ^{1}H NMR spectrum (Fig. 1) was assigned as follows on the basis of the 2D ^{1}H COSY NMR spectrum: a singlet at 1.45 ppm was assigned to the *tert*-butyl protons. The doublets with *J* 8.8 Hz at 6.60 and 7.95 ppm were assigned to H_g and H_h, the doublets with *J* 2.0 Hz at 7.32 and 8.12 ppm were assigned to H_a and H_b and the doublets with *J* 7.3 Hz at 7.55 and 8.14 ppm were assigned to H_c and H_f. The triplets with *J* 7.3 Hz at 7.37 and 7.45 ppm were assigned to H_d and H_e. On the other hand, the absorption due to the 1-phenyl protons (H_i) was observed as a broad signal spread over 6.7–7.6 ppm. As discussed below, this broadening is due to the occurrence of an unpaired electron in the phenyl group. On the basis of the above spectroscopic results and the satisfactory elemental analysis the compound was identified to be **5**.

Radicals **2a** and **2b** gave nearly identical results, (Scheme 3). Thus, upon heating at 80 °C for 28 h, **2a** almost completely decomposed to give **7a** and **8a** in 49 and 48% yields, respectively, and upon heating for 30 h **2b** almost completely decomposed to give **7b** and **8b** in 43 and 48% yields, respectively. Their structures were confirmed on the basis of the IR, ^{1}H NMR and mass spectra and the elemental analyses.

The decomposition mechanism of **1a** is shown in Scheme 2. An intramolecular homolytic attack of the nitrogen radical centre to one of the *ortho* positions of the 2- and 6-phenyl

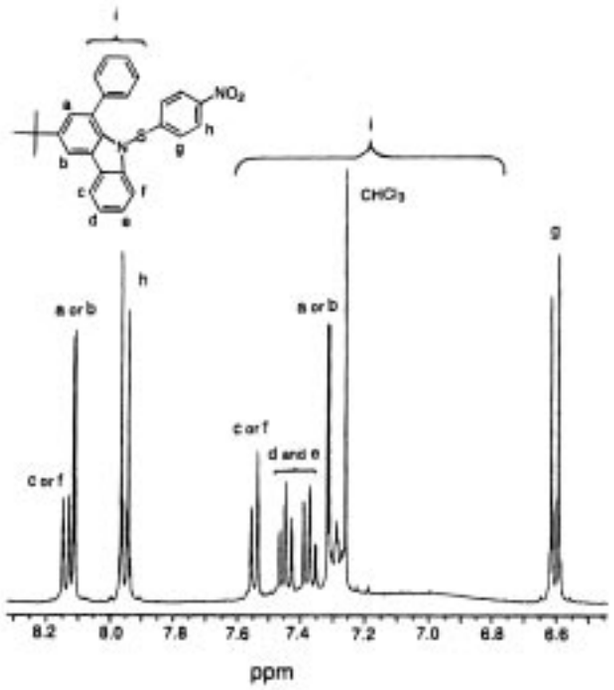
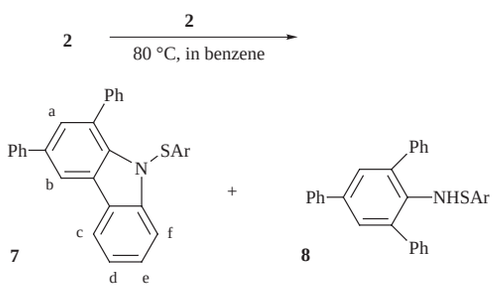


Fig. 1 ^{1}H NMR spectrum of **5**. Expansion of the aromatic region is shown.



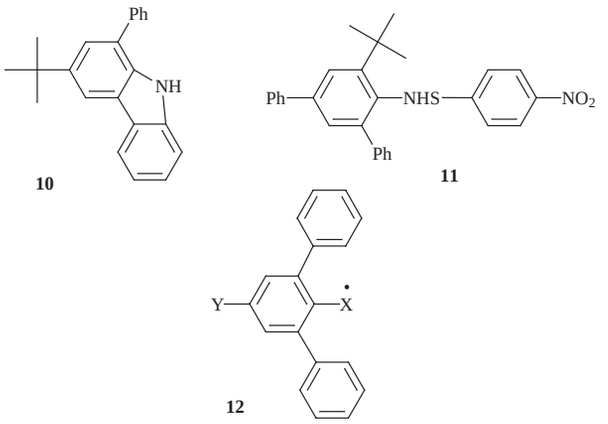
a Ar = 4-$NO_2C_6H_4$
b Ar = 2, 4-$Cl_2C_6H_3$

Scheme 3

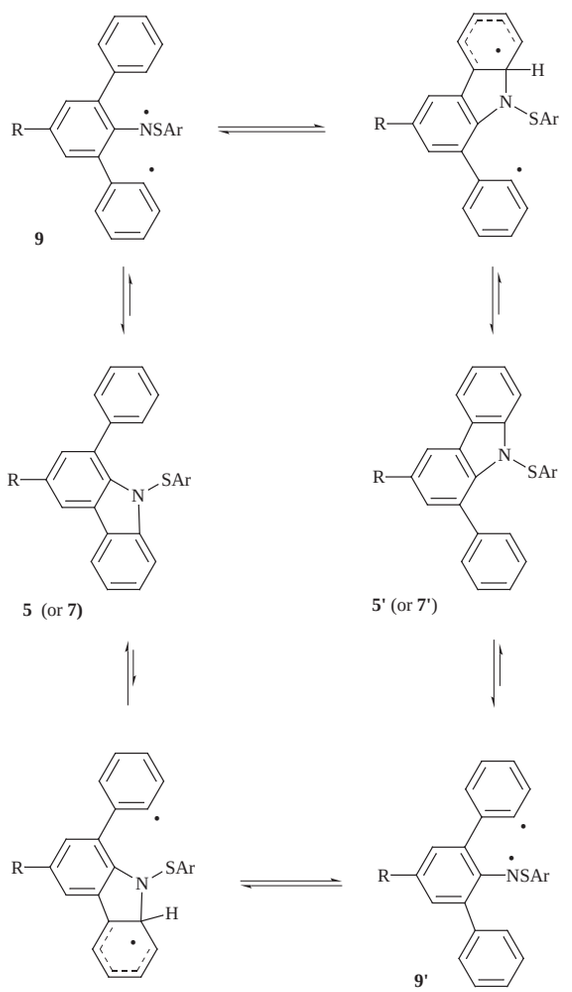
group yields an intermediate cyclohexadienyl radical **4**. Disproportionation between **4** and **1a** gives an equivalent amount of **5** and **6**. The formation of **7** and **8** can be rationalized in terms of the same mechanism.

Although homolytic aromatic substitution of transient radicals such as phenyl, methyl and benzoyloxyl radicals are well established,[12] it is surprising that stable free radicals such as **1** and **2** undergo homolytic aromatic substitution. The EPR study for **1**–**3** showed the spin densities on the 2- and 6-phenyl groups are nearly zero. We assume that the reason why such a homolytic aromatic substitution can occur in **1** and **2** is that it is an intramolecular reaction favourable in entropy. Of course, we confirmed that a homolytic aromatic substitution between **1** or **2** and benzene used as the solvent never occurs even at high temperatures.

As mentioned above, the ^{1}H NMR spectra of **5** and **7** gave a broad signal for the 1-phenyl protons (H_i), as found in Fig. 1. However, the broad signal became more and more sharp with a lowering in temperature and at −50 °C considerably sharp NMR signals were observed. Such a broadening does not occur in the ^{1}H NMR spectra of carbazole itself and 1-phenyl-3-*tert*-butylcarbazole **10**. When molecules are contaminated with paramagnetic species or molecules are partly converted to paramagnetic species by oxidation or bond homolysis, a significant line broadening is observed in the NMR measurements because a strong magnetic interaction between the unpaired electron spin and protons reduce the relaxation times of pro-



tons. It is speculated that there is a slow interconversion between **5** and **5′** and between **7** and **7′** at room temperature, as shown in Scheme 4. A homolytic cleavage of the C–N bond in



R = Bu^t (**5**) or Ph (**7**)

Scheme 4

the carbazole ring yields an aminyl and phenyl biradical. The aminyl radical centre intramolecularly attacks the remaining phenyl group to yield a cyclohexadienyl radical. In phenyl and cyclohexadienyl radicals the unpaired electron spin strongly interacts with protons, as indicated by the large a_H value.†,[13,14] It is speculated that the broadening of the phenyl protons in the NMR spectra of **5** and **7** is due to the formation of phenyl and cyclohexadienyl radicals.

To detect the intermediate radicals, the EPR measurements of a benzene solution of **5** were carried out at room temperature, and a 1:1:1 triplet with $a_N = 0.934$ mT and $g = 2.0055$ was detected. Since the a_N and g values are the same as those for **1** ($a_N = 0.932$ mT; $g = 2.0055$),[11] the radical observed was identified as **1**. It seems that this radical is formed by hydrogen-atom abstraction by **9** from hydrogen donors.

Thioaminyl **3a** showed a quite different behaviour for the thermal stability. Upon heating for one day at 80 °C, the characteristic blue colour due to **3a** remained strong, and for almost complete disappearance, a further 7 days, at least, were required. TLC analysis showed formation of at least six compounds, and only **11** could be isolated in 48% yield by the preparative GPC method.

Why is only **3a** so persistent at high temperature? The reason lies in its particular structure. First, one of the *ortho* positions is occupied by a *tert*-butyl group which is inert towards hydrogen-atom abstraction. Secondly, the phenyl group attached to the remaining *ortho* position is twisted by 87° from the anilino benzene ring, as indicated by the X-ray crystallographic analysis.[11] This great twisting of the phenyl group makes intramolecular homolytic attack by the nitrogen radical centre very difficult. On the other hand, **1a** and **2b** are shown to adopt a different conformation by the X-ray crystallographic analyses.[9,11] Although one of the *ortho* phenyl groups is certainly seriously twisted from the anilino benzene ring by 64 (**1a**) or 87° (**2b**), the remaining phenyl group is only twisted by 45 (**1a**) or 49° (**2b**). At this angle, it is possible for intramolecular homolytic attack by the nitrogen radical centre to occur. Accordingly, if the *ortho* positions of the 2- and 6-phenyl groups are protected from such a reaction, the resulting radicals may become thermally very stable.

Conclusions

We have investigated the thermal decomposition of **1**–**3** and found that decomposition takes place *via* an intramolecular homolytic aromatic substitution reaction. Accordingly, when radicals have a structure represented by **12**, an identical decomposition reaction may take place, even though they are quite stable and isolable radicals.

Experimental

All mps were determined on a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were run for samples as KBr pellets on a JASCO A-202 spectrophotometer. ^{1}H NMR spectra were recorded with a JEOL α-400 spectrometer (400 MHz) with $SiMe_4$ as internal standard; *J* values are given in Hz. Mass spectra were taken with JEOL JMS-HX 100 spectrometer at 70 eV using a direct inlet system. Isolation of the products was performed on an LC-908 recycling preparative HPLC (Japan Analytical Industry Co., LTD) using chloroform as the eluent. TLC analyses were carried out on Merck 60 F_{254} neutral aluminium oxide sheets. Thioaminyl radicals **1a**, **2a**, **2b** and **3a** were prepared by previous methods.[9–11]

Thermal decomposition of 1, 2 and 3 in benzene

Thioaminyl radical crystals (0.265 mmol) and benzene (20 cm^3) were put in a glass tube. The glass tube was then degassed by freeze–pump–thaw cycles and sealed off from the vacuum system. The glass tube was immersed in a water-bath kept at 80 °C until the characteristic purple (**1a**), yellowish green (**2a**), bluish green (**2b**) or blue colour (**3a**) almost completely disappeared. The solvent was evaporated under reduced pressure and the resulting residue was subjected to preparative GPC. The yields of the products were determined by weight. Compounds **6**, **8a**, **8b** and **11** were identified by comparison of the IR and ^{1}H

† The a_H values for phenyl and cyclohexadienyl radicals are reported to be 1.74 (*o*-H), 0.59 (*m*-H), 0.19 (*p*-H) and 0.913 (1- and 5-H), 0.264 (2- and 4-H), 1.356 (3-H), 4.81 mT (6-H), respectively.

NMR spectra with the authentic samples. The structures of **5**, **7a** and **7b** were determined on the basis of IR, ^{1}H NMR and mass spectra and elemental analyses.

***N*-(4-Nitrophenylthio)-1-phenyl-3-*tert*-butylcarbazole 5**
Yield 50% (60.0 mg, 0.133 mmol), yellow micro prisms (MeOH); mp 80–83 °C; *m*/*z* 452 (M^+, 41%), 299 (50), 284 (100), 242 (96) and 57 (33); $\delta_H(CDCl_3)$ 1.45 (9 H, s, Bu^t), 6.60 (2 H, d, *J* 8.8, H_g), 6.7–7.6 (5 H, br s, H_i), 7.32 (1 H, d, *J* 2.0, H_a or H_b), 7.37 (1 H, t, *J* 7.3, H_d or H_e), 7.45 (1 H, t, *J* 7.3, H_d or H_e), 7.55 (1 H, d, *J* 7.3, H_c or H_f), 7.95 (2 H, d, *J* 8.8, H_h), 8.12 (1 H, d, *J* 2.0, H_a or H_b) and 8.14 (1 H, d, *J* 7.3, H_c or H_f) (Found: C, 74.24; H, 5.39; N, 6.16. $C_{28}H_{24}N_2O_2S$ requires C, 74.30; H, 5.36; N, 6.19%).

***N*-(4-Nitrophenylthio)-4-*tert*-butyl-2,6-diphenylaniline 6**
Yield 43% (52.1 mg, 0.115 mmol), yellow plates (EtOH); mp 148–149 °C (lit.,[11] 146–148 °C).

***N*-(4-Nitrophenylthio)-1,3-diphenylcarbazole 7a**
Yield 49% (62.0 mg, 0.131 mmol), yellow micro prisms (MeOH); mp 93–96 °C; *m*/*z* 472 (M^+, 4.4%) and 319 (100); $\delta_H(CDCl_3)$ 6.61 (2 H, d, *J* 8.8, *o*-H of SAr), 6.8–7.6 (5 H, br s, 2-Ph), 7.37–7.50 (5 H, m, H_d, H_e and *m*- and *p*-H of 3-Ph), 7.54 (1 H, d, *J* 2.0, H_a or H_b), 7.60 (1 H, d, *J* 7.3, H_c or H_f), 7.74 (2 H, d, *J* 7.3, *o*-H of 3-Ph), 7.97 (2 H, d, *J* 8.8, *m*-H of SAr), 8.18 (1 H, d, *J* 7.3, H_c or H_f) and 8.33 (1 H, d, *J* 2.0, H_a or H_b) (Found: C, 76.20; H, 4.31; N, 5.89. $C_{30}H_{20}N_2O_2S$ requires C, 76.24; H, 4.27; N, 5.93%).

***N*-(4-Nitrophenylthio)-2,4,6-triphenylaniline 8a**
Yield 48% (60.9 mg, 0.128 mmol), yellow prisms (EtOH–benzene); mp 148–149 °C (lit.,[9] 149–150 °C).

***N*-(2,4-Dichlorophenylthio)-1,3-diphenylcarbazole 7b**
Yield 43% (56.2 mg, 0.113 mmol), colorless prisms (MeOH–ethyl acetate); m 145–146 °C; *m*/*z* 497 (11%), 496 (5), 495 (M^+, 14) and 319 (100); $\delta_H(CDCl_3)$ 6.05 (1 H, d, *J* 8.8, *o*-H of SAr), 6.6–7.6 (5 H, br s, 1-Ph), 6.91 (1 H, dd, *J* 8.8 and 2.0, *m*-H of SAr), 7.22 (1 H, d, *J* 2.0, *m*-H of SAr), 7.33–7.50 (5 H, m, H_d, H_e and *m*- and *p*-H of 3-Ph), 7.53 (1 H, d, *J* 2.0, H_a or H_b), 7.60 (1 H, d, *J* 7.8, H_c or H_f), 7.73 (2 H, d, *J* 8.3, *o*-H of 3-Ph), 8.17 (1 H, d, *J* 7.8, H_c or H_f) and 8.32 (1 H, d, *J* 2.0, H_a or H_b) (Found: C, 72.32; H, 4.13; N, 2.55. $C_{30}H_{19}Cl_2NS$ requires: C, 72.57; H, 3.87; N, 2.82%).

***N*-(2,4-Dichlorophenylthio)-1,3-diphenylaniline 8b**
Yield 48% (64.3 mg, 0.129 mmol), colorless needles (EtOH–benzene); mp 144–145 °C (lit.,[9] 142–143 °C).

***N*-(4-Nitrophenylthio)-2-*tert*-butyl-2,4-diphenylaniline 11**
Yield 48% (57.8 mg, 0.127 mmol), yellow plates (EtOH); mp 157–159 °C (lit.,[11] 158–160 °C).

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