Mass Spectrometric Determination of Spin Adducts of Hydroxyl and Aryl Free Radicals

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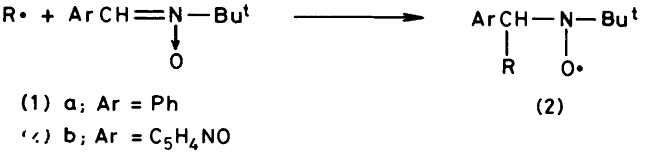
G.l.c.–mass spectrometry has been applied in conjunction with e.s.r. to the identification of spin adducts produced by reactions between short-lived free radicals and nitrone spin traps. Thermally unstable spin adducts were converted into thermally stable and volatile trimethylsilyl derivatives suitable for g.l.c.–mass spectrometry. The structures of the trimethylsilylated spin adducts could be determined by observing molecular and fragment ion peaks as well as isotope peaks. Hydroxyl and aryl free radicals are identifiable by this method. Even if there were more than two different kinds of spin adduct, they could be easily separated by g.l.c. and identified by their mass spectra.

Spin trapping[1] has been applied recently to many fields of chemistry such as polymerization,[2] radiation chemistry,[3] biochemistry,[4] organic chemistry,[5] and solution chemistry.[6] Usually structural information about the spin adducts was obtained from e.s.r. measurements. However, difficulties can arise in the identification of the spin adducts generated in the spin trapping reaction because the e.s.r. spectra are often insensitive to the nature of adding radicals in the case of nitrone spin traps or liable to be complex in cases of nitroso spin traps. Thus other methods are needed in order to identify spin adducts confidently. Hatano and his co-workers have developed radical chromatography for this purpose, in which they make use of h.p.l.c. to identify spin adducts.[7] We considered that g.l.c.–mass spectrometry would provide another method for identification of the spin adducts.

The mass spectra of numerous pyrrolidine-*N*-oxyl[8] and piperidine-*N*-oxyl[9] free radicals (spin labels[10]) have already been studied. It has been shown that mass spectroscopic information concerning molecular and fragment ions can be useful for the identification of these relatively stable radicals. Since the structures of the spin adducts derived from nitrones or nitroso compounds are similar to those of spin labels (in that the nitroxyl moiety is blocked by bulky substituents and is shielded from the attack by some reagents), measurements of mass spectra of such spin adducts are expected to be possible.

Spin adducts of *N*-t-butylbenzylideneamine *N*-oxide (1a) and *N*-t-butyl-(1-oxidopyridinium-4-yl)methyleneamine *N*-oxide (1b) are reported to be stable under the usual experimental conditions.[11] On the other hand, the corresponding adducts (2) are considered to be less stable thermally than spin labels because they have a hydrogen atom on the carbon atom adjacent to the nitroxyl function,[12] and afford the corresponding nitrone (3) and hydroxylamine (4) by disproportionation in some cases. Either or both of the disproportionation products may undergo further chemical reaction.

We describe here a new method for the identification of spin adducts by g.l.c.–mass spectrometry, with the aid of mass chromatography. Nitrones were used as spin traps in this investigation because their free radical adducts were shown to be more stable both thermally and photochemically than those from nitroso compounds. In favourable cases, the spin adducts are stable enough to show good mass spectra. In many cases, however, spin adducts are so unstable under the conditions for electron impact mass spectrometry that their molecular ion peaks cannot be observed. Some of them tend to decompose even under the conditions for g.l.c. separation. Even such thermally unstable spin adducts can be analysed by g.l.c.–mass spectrometry when they are converted into trimethylsilyl derivatives, which have considerable thermal stability and volatility. Trimethylsilylation usually proceeds on the nitroxyl oxygen atom of spin adduct (5).† When the spin adducts have groups containing active hydrogen atoms ($^-$OH, $^-$NH$_2$, $^-$CO$_2$H, $^-$SH),[13] these active hydrogen atoms are also replaced by the trimethylsilyl moiety, forming bis- or tris-(trimethylsilyl) derivatives.



$$\mathrm{R\cdot + ArCH{=}\overset{\displaystyle N}{\underset{\displaystyle O}{\downarrow}}{-}Bu^t \longrightarrow ArCH(R){-}N(O\cdot){-}Bu^t}$$

(1) a; Ar = Ph
(1) b; Ar = C_5H_4NO

(2)

Experimental

Spin Traps.—The nitrones (1a)[14] and (1b)[15] were prepared according to known methods. Nitroso spin traps (nitrosobenzene, nitrosodurene) were also used in the experiments. However, owing to their tendency to dimerize or undergo photolysis, and the instability of the spin adducts, a g.l.c.–mass spectrometric analysis was not successfully made.

Generation of Radicals.—Hydroxyl and aryl radicals were generated in the presence of the spin traps in order to carry out the addition reaction *in situ*.

Hydroxyl radicals were produced by the reaction of $Na_2S_2O_8$ or $(NH_4)_2S_2O_8$ with H_2O.[16] Aqueous sodium peroxodisulphate or ammonium peroxodisulphate (10^{-2} mol l^{-1}) containing the nitrone (1b) (10^{-1} mol l^{-1}) was set aside for 24—48 h. After the reaction, the solvent was distilled off *in vacuo*, and the residue was dried and treated with the trimethylsilylating agent (see below).

Aryl radicals were generated either by thermal decomposition of a substituted phenylazotriphenylmethane (PAT) or by

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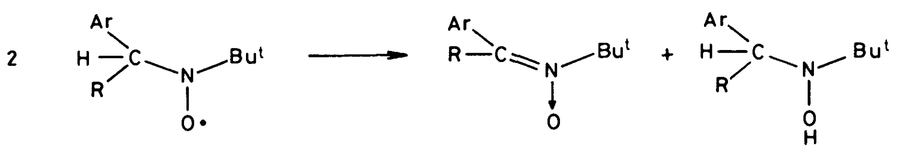
† The mechanism of trimethylsilylation on the nitroxyl oxygen is not certain. The nitroxyl radical was shown by e.s.r. spectroscopy to be consumed in reaction with the trimethylsilylating reagent. Reaction may proceed *via* direct abstraction of the trimethylsilyl group by the nitroxyl, but the alternative path involving initial formation of the corresponding hydroxylamine by disproportionation and successive heterolytic trimethylsilylation cannot be excluded.



(2) (3) (4)

$$\mathrm{Ar-\underset{R}{CH}-\underset{O^{\bullet}}{N}-Bu^t \longrightarrow Ar-\underset{R}{CH}-\underset{O-SiMe_3}{N}-Bu^t}$$

(2) (5)

photochemical decomposition of halogen-substituted arenes. Substituted PATs were synthesized by the method of Cohen and Wang.[17] A solution of substituted PAT (6) (10^{-3} mol l^{-1}) in benzene (5 ml) was decomposed in the presence of the nitrone (1a) (10^{-3} mol l^{-1}) at 80 °C for 3 min, and then oxygen was passed through in order to remove triphenylmethyl radical.[18]

$$\underset{(6)}{\mathrm{Ar-N{=}N-CPh_3}} \xrightarrow{\text{heat}} \mathrm{Ar^{\bullet} + N_2 + {}^{\bullet}CPh_3}$$

$$\mathrm{Ar^{\bullet}} + (1a) \longrightarrow (2a)$$

$$\mathrm{2CPh_3^{\bullet}} \xrightarrow{O_2} \mathrm{Ph_3COOCPh_3}$$

Alternatively, a solution (20 ml) of halogen-substituted arene (0.1 mol l^{-1}) in benzene was irradiated with a 10 W low-pressure mercury lamp in the presence of the nitrone (1a) (0.1 mol l^{-1}). The solution was previously freed from O_2 by bubbling N_2 for 10 min. On irradiation, halogen–carbon bond fission took place producing aryl radicals. In both cases the solvent was distilled off and the residue was trimethylsilylated.

Trimethylsilylation of Spin Adducts.—*N*,*O*-Bis(trimethylsilyl)acetamide was used as the trimethylsilylating agent for the adducts of (1a) with aryl radicals. Reactions were carried in a 1 ml tapered reaction vial sealed with a Teflon-faced rubber disc. A small portion (*ca.* 1 mg) of crude product containing the spin adduct was transferred into a reaction vial and dried *in vacuo* for about 6 h. Then *ca.* 1 ml of trimethylsilylating reagent was added to the vial and the mixture was set aside for 12 h. All operations in the trimethylsilylation procedure were performed under dry nitrogen in a dry box. A similar procedure with hexamethyldisilazane gave the bistrimethylsilyl derivative of the adduct of hydroxyl radical with the nitrone (1b).

General Procedure and Apparatus for E.s.r. and G.l.c.–Mass Spectrometric Measurement.—Solutions of spin adducts were degassed by bubbling dry nitrogen for at least 10 min before e.s.r. measurement. The spectra were recorded with a JEOL-FE1X spectrometer. G.l.c.–mass spectrometric measurements of spin adducts were carried out with a Shimadzu LKB 9000B spectrometer. In the g.l.c. separation process, a mass chromatographic method was applied in order to identify the g.l.c. peaks of spin adducts. The g.l.c. conditions were as follows: (a) bistrimethylsilylated hydroxyl adduct of (1b), 2% OV-1 on Chromosorb (60—80 mesh) 3 m × 2 mm, column temp. 70 °C (held 1 min) to 240 °C (at 20 °C min^{-1})' inj. temp. 220 °C; (b) aryl adducts of (1a), 2% OV-17 on Chromosorb (60—80 mesh) 2 m × 3 mm, column temp. 120 °C (held 1 min) to 300 °C (at 20 °C min^{-1}), inj. temp. 300 °C. In the mass chromatographic measurements, the mass spectra were measured every 6 s with the sample gas introduced into the ion source from the gas chromatograph. Spectra taken at the steep slope of the chromatogram are considerably deformed and the relative intensities of the peaks are unreliable, even when the spectra are scanned rapidly. Quantitative analyses of adducts were therefore carried out from the gas chromatogram. In order to check the reliability of mass spectra, the intensities of some important peaks were determined by use of a selective ion monitor.

Results and Discussion

Hydroxyl Adduct of the Nitrone (1b).—We carried out a g.l.c.–mass spectrometric measurement of the hydroxyl adduct (7) of (1b) in addition to the e.s.r. measurement (a_N = 14.68 G, $a_H{}^{\beta}$ = 1.68 G in H_2O). From comparing these hyperfine values with reported values,[16] this radical species is thought to be an OH adduct of (1b). However, no mass spectral evidence in favour of the presence of a hydroxyl spin adduct was obtained when the (1b) adduct was injected without further derivatization. The result is reasonably explained by the fact that the hydroxyl spin adduct of (1b) is unstable and decomposes in the process of g.l.c. separation. The spin adduct was therefore trimethylsilylated in order to convert it into a more stable and volatile derivative suitable for g.l.c.–mass spectrometric measurement. The intensity of the e.s.r. signal of the hydroxyl spin adduct is greatly diminished after trimethylsilylation (about 1/20th of the original). This provides evidence that trimethylsilylation occurs on the nitroxyl oxygen, forming the diamagnetic bistrimethylsilylated species (8).

The mass spectrum is shown in Table 1. The g.l.c. peak corresponding to the bistrimethylsilylated hydroxyl spin adduct had a retention time of 18.1 min. The molecular ion M^+ (*m*/*z* 356) peak appeared with low intensity. Fragment ions such as $[M - CH_3]^+$ (*m*/*z* 341), $[M - Bu^t]^+$ (*m*/*z* 299), $[M - Me_3Si]^+$ (*m*/*z* 283), $[M - Me_3Si - Bu^t]^+$ (*m*/*z* 226), and $[M - Me_3Si - Bu^t - H]^+$ (*m*/*z* 225, base peak) reasonably explain the structure of the bistrimethylsilylated hydroxyl spin adduct. Other strong peaks are those with mass numbers 281 and 221. The former seems to be produced by elimination of H_2O from $[M - Bu^t]^+$. The latter might be formed by degradation of the former fragment. In addition, ions at *m*/*z* 147 $[Me_3Si{=}O{-}SiMe_3]^+$,[19] characteristic of trimethylsilylated polyhydroxy compounds, and *m*/*z* 73 $[Me_3Si]^+$ [20] were observed.

From the mass spectral data, the trimethylsilylated hydroxyl adduct of (1b) was identified confidently. The method was shown to be applicable, by use of the trimethylsilylation technique, to thermally unstable spin adducts.

Aryl Adducts of the Nitrone (1a).—An earlier paper [21] on the e.s.r. spectra of substituted phenyl adducts of (1a) reported that $a_H{}^{\beta}$ is dependent on the position of the substituents on the benzene ring, while a_N is nearly constant.

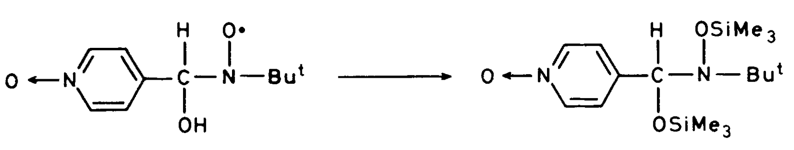

(7) (8)

Table 1. Mass spectrum of bistrimethylsilylated hydroxyl spin adduct of the nitrone (1b)

	Fragment	Mass	Relative intensity (%)
(A)	$M^{+\cdot}$	356	9
(B)	$[M - H]^+$	355	25
(C)	$[M - Me]^+$	341	10
(D)	$[M - Bu^t]^+$	299	67
(E)	$[M - Me_3Si]^+$	283	9
(F)	$[(D) - H_2O]^+$	281	70
(G)	$[(E) - Bu^t]^{+\cdot}$	226	23
(H)	$[(E) - Bu^t\text{-}H]^+$	225	100
(I)	$[(F) - 60]^+$	221	52
(J)	$[Me_2Si{=}O{-}SiMe_3]^+$	147	31
(K)	$[Me_3Si]^+$	73	7

Table 2. Hyperfine splitting constants[a] of adducts of the nitrone (1a) with various aryl radicals in benzene

(a) Produced by photolysis of corresponding halogenoarenes

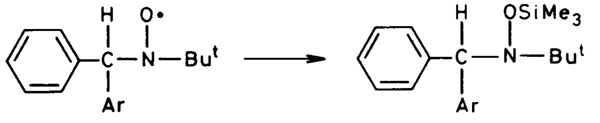
Halogenoarene	Free radical	a_N/G	$a_H{}^{\beta}$/G
o-BrCl	2-ClC$_6$H$_4$	14.5	2.92
m-BrCl	3-ClC$_6$H$_4$	14.5	2.17
p-BrCl	4-ClC$_6$H$_4$	14.5	2.14
o-Cl$_2$	2-ClC$_6$H$_4$	14.5	2.90
m-Cl$_2$	3-ClC$_6$H$_4$	14.5	2.17
p-Cl$_2$	4-ClC$_6$H$_4$	14.5	2.15
o-Br$_2$	2-BrC$_6$H$_4$	14.5	2.96
m-Br$_2$	3-BrC$_6$H$_4$	14.5	2.15
p-Br$_2$	4-BrC$_6$H$_4$	14.5	2.17
1,2,3-Cl$_3$	2,6-Cl$_2$C$_6$H$_3$	14.4	7.37
	2,3-Cl$_2$C$_6$H$_3$	14.4	2.79
1-Br-2,6-Cl$_2$	2,6-Cl$_2$C$_6$H$_3$	14.5	7.39
1,3-Br$_2$-2-Cl	3-Br-2-ClC$_6$H$_3$	14.5	2.85
1-Br-2,3-Cl$_2$	2,3-Cl$_2$C$_6$H$_3$	14.4	2.81
1-Bromo-naphthalene	1-Naphthyl	14.5	3.56

(b) Produced by the pyrolysis of arylazotriphenylmethanes

Free radical	a_N/G	$a_H{}^{\beta}$/G
C$_6$H$_5$	14.5	2.18
4-ClC$_6$H$_4$	14.5	2.15
4-BrC$_6$H$_4$	14.5	2.15
4-NO$_2$C$_6$H$_4$	14.5	2.17
4-MeC$_6$H$_4$	14.4	2.15
2-ClC$_6$H$_4$	14.5	2.89

[a] ±0.02G.

Values of $a_N{}^{\beta}$ of spin adducts of aryl radicals carrying substituents at the *meta*- or *para*-position are nearly constant ($a_H{}^{\beta}$ = 2.1 G), while *ortho*-substituted aryl spin adducts show larger $a_H{}^{\beta}$ values (2.8—3 G). Our e.s.r. measurements on aryl spin adducts in benzene have revealed a similar tendency (Table 2). From these results, it is possible to distinguish *ortho*-substituted from *meta*- and *para*-substituted aryl radicals. However, further information on the nature of the substituents on the benzene ring cannot be obtained from the e.s.r. spectra.


(9) (10)

In order to characterize the aryl spin adducts individually, g.l.c.–mass spectrometry was applied. The g.l.c. peaks of the aryl adducts of (1a) could not be assigned by mass chromatography when the adduct solution was injected directly. However, trimethylsilylation of the spin adducts (9) enabled us to perform g.l.c.–mass spectrometric analysis.

The mass spectra of various trimethylsilylated aryl spin adducts (10) are shown in Table 3. In contrast to that of the hydroxyl spin adduct, the molecular ion M^+ was not observed. This might be due to easy elimination of the t-butyl moiety; α-cleavage [22] of a silyl ether is known to occur easily when the α-carbon atom is branched. As shown in Table 3, trimethylsilylated adducts of (1a) and aryl radicals are degraded through a common pathway, producing $[M - 57]^+$, $[M - 58]^+$, $[M - 73]^+$, and $[M - 147]^+$ peaks, assigned to $[M - C_4H_9]^+$, $[M - C_4H_{10}]^+$, $[M - C_5H_{13}]^+$, and $[ArPhC{=}N]^+$, respectively, by high resolution measurements.[23] Isotope peaks of the halogen (chlorine or bromine) atoms appeared as expected. [*] From the fragmentation patterns and appearance of isotope peaks of the trimethylsilyl derivatives, these spin adducts can be identified unambiguously.

In the cases of the 2-halogenophenyl spin adducts, there appeared fragment ions produced by elimination of the halogen atom from $[M - 73]^+$ in addition to the fragment ions common to all aryl spin adducts noted above. Markedly different behaviour of 2-halogenophenyl spin adducts was also observed in the gas chromatogram, which showed two closely adjacent g.l.c. peaks. The high resolution spectra showed coincident peaks, suggesting the formation of a pair of stereoisomers (presumably diastereoisomers) in the process of trimethylsilylation. In the trimethylsilylated 2-halogenophenyl spin adducts, rotation around either or both of the skeletal C–N–O bonds is thought to be restricted (as shown by molecular models), by interaction between the halogen atom and the bulky t-butyl and trimethylsilyl group(s). Since a chiral α-carbon atom is present in the spin adduct, restricted rotation would lead to formation of a pair of diastereoisomers [24] corresponding to the two g.l.c. peaks. The same behaviour was observed in the cases of the 2,6-dichlorophenyl, 2,3-dichlorophenyl, and naphthyl spin adducts of (1a).

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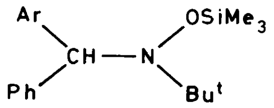
[*] The intensity ratios of the isotope peaks were not always consistent with theoretical values. The discrepancy came from the measurement by mass chromatography. When the sampling (carried out every 6 s automatically) was performed at a point where the gas chromatogram shows a steep gradient, the intensity ratio can deviate from the theoretically expected value since the amount of the sample introduced varies considerably during the mass spectral measurement. In these cases, the peak area ratios of the isotope peaks were determined by selective ion monitoring (SIM); the results agreed with theoretical values. The intensity ratios from SIM are given in parentheses in Table 3.

Table 3. G.l.c.–mass spectra of the trimethylsilylated adducts of the nitrone (1a) with various aryl radicals



				Relative intensity (%)[b]						
Ar˙	Radical source	Method of generation	G.l.c. retention[a] time (min)	$[M - 57]^+$ (A)	$[M - 58]^+$ (B)	$[M - 73]^+$ (C)	$[M - 147]^+$ (D)	$[75]^+$ $HO{=}SiMe_2^+$	$[73]^+$ $SiMe_3^+$	Other peak(s)
C_6H_5˙	PAT[c]	Thermolysis	7.7	7	35	15	100		7	
4-$CH_3C_6H_4$˙	MePAT[c]	Thermolysis	6.6	10	36	12	100		8	
4-$NO_2C_6H_4$˙	NO_2PAT[c]	Thermolysis	9.2	6	14	24	100	8	36	
4-ClC_6H_4˙	4-BrC_6H_4Cl	Photolysis	9.3	7	26 9*	13 5*	100 (100)[d] 51* (32)*	10	12	
	4-ClC_6H_4Cl	Photolysis	9.0		23 9*	16 4*	100 39*		17	
	ClPAT[c]	Thermolysis	9.4		12 4*	13 5*	100 37*	19	17	
4-BrC_6H_4˙	4-BrC_6H_4Br	Photolysis	9.1	12 8*	28 30*	18 20*	92 100*		7	
	BrPAT[c]	Thermolysis	9.2	8 6*	22 24*	15 17*	92 100*	10	12	
3-ClC_6H_4˙	3-BrC_6H_4Cl	Photolysis	9.0	15	45 16*	40 15*	100 37*	9	13	
	3-ClC_6H_4Cl	Photolysis	8.9	4	40 13*	14 6*	100 36*		6	

Table 3 (*continued*)

			G.l.c.	Relative intensity (%)[b]						
Ar$^{\cdot}$	Radical source	Method of generation	retention[a] time (min)	$[M-75]^+$ (A)	$[M-58]^+$ (B)	$[M-73]^+$ (C)	$[M-147]^+$ (D)	$[75]^+$ HO=SiMe$_2^+$	$[73]^+$ SiMe$_3^+$	Other peak(s)
3-BrC$_6$H$_4^{\cdot}$	3-BrC$_6$H$_4$Br	Photolysis	9.2	10	29	19	100	9	14	
				8*	30*	17*	95*			
2-ClC$_6$H$_4^{\cdot}$	2-BrC$_6$H$_4$Cl	Photolysis	8.0	5	33	31	100	17	23	40 [(C) − Cl]$^+$
					14*	11*	37*			
			8.4	5	30	31	100	20	17	45 [(C) − Cl]$^+$
					11*	10*	39*			
	2-ClC$_6$H$_4$Cl	Photolysis	8.4		39	24	100	4	2	39 [(C) − Cl]$^+$
					15*	9*	40*			
			8.7	14	35	23	100	11		32 [(C) − Cl]$^+$
				5*	14*	8*	41*			
2-BrC$_6$H$_4^{\cdot}$	2-BrC$_6$H$_4$Br	Photolysis	9.3	8	21	20	100		7	74 [(C) − Br]$^+$
				8*	22*	20*	100*			
			9.8	7	14	15	100	7		64 [(C) − Br]$^+$
				4*	18*	16*	92*			
2,6-Cl$_2$C$_6$H$_3^{\cdot}$	1-Br-2,6-Cl$_2$C$_6$H$_3$	Photolysis	9.8		70	71	100 (100)[d]	34	67	30 [(C) − Cl]$^+$
				12*	59*	60*	97* (70)*			12* [(C) − Cl]$^+$
					10**	13**	37** (15)**			
			10.4	9	34	39	100	3	21	9 [(C) − Cl]$^+$
				6*	20*	27*	83*			3* [(C) − Cl]$^+$
						5**	15**			
2,3-Cl$_2$C$_6$H$_3^{\cdot}$	1,2,3-Cl$_3$C$_6$H$_3$	Photolysis	10.0	8	22	27	100	7	19	9 [(C) − Cl]$^+$
				5*	14*	19*	63*			3* [(C) − Cl]$^+$
					3**	3**	10**			
			10.6	6	19	27	100	13	17	11 [(C) − Cl]$^+$
				5*	12*	19*	83*			3* [(C) − Cl]$^+$
					4**	5**	17**			
1-Naphthyl	1-BrC$_{10}$H$_7$	Photolysis	9.2	9	30	4	100	11	21	54 [C$_{10}$H$_7$]$^+$
			9.8	8	26	4	100	14	30	82 [C$_{10}$H$_7$]$^+$

[a] G.l.c. conditions: see Experimental section. [b] Figures labelled * and ** denote the intensities of isotope peaks, $(P + 2)^+$ and $(P + 4)^+$, respectively. [c] PAT = PhN$_2$CPh$_3$; MePAT = 4-MeC$_6$H$_4$N$_2$CPh$_3$; NO$_2$PAT = 4-NO$_2$C$_6$H$_4$N$_2$CPh$_3$; ClPAT = 4-ClC$_6$H$_4$N$_2$CPh$_3$; BrPAT = 4-BrC$_6$H$_4$N$_2$CPh$_3$. [d] Values obtained by SIM in parentheses.

In conclusion, g.l.c.–mass spectrometry is of great use for the identification of spin adducts. Mass spectroscopic information concerning molecular ions, fragment ions, and their isotope peaks helps to identify the trapped free radical. Moreover, this method enables us to separate several coexisting spin adducts and to identify different kinds in the same run.[23] The method may extend the application of spin trapping in various fields such as organic chemistry and environmental chemistry.[25]

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