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MASS SPECTROMETRIC DETERMINATION OF SPIN ADDUCTS IN SPIN TRAPPING TECHNIQUE

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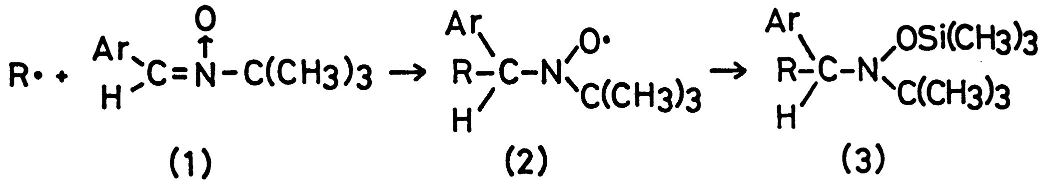
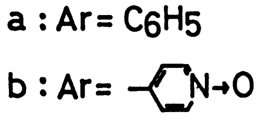
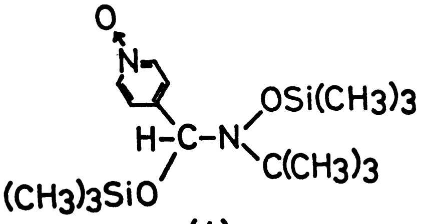
The GC/MS(MC) technique was shown to be applicable to identify various kinds of free radicals trapped by α-aryl *N*-*t*-butyl nitrones. When spin adducts are unstable under the conditions for measurement, they were trimethylsilylated on the nitroxyl oxygen atom, which makes GC/MS measurement possible.

Since the technique of spin trapping was first introduced by Janzen's group,1) it has been applied to prove the presence of free radicals in solution.2) It makes use of a diamagnetic spin trap which reacts with a free radicals giving rise to another relatively stable, ESR-observable free radical called spin adduct. Most common spin traps are the compounds designed to produce nitroxide radicals on reacting with free radicals.3) The typical example of them is either a nitrone or a nitroso compound. In the case of spin adducts (2) of nitrones (1), the ESR hyperfine splitting constants (a_N and a_β^H) are rather insensitive to the nature of added free radicals when the conformation of the spin adduct is similar.

Now, another method for the detection of spin adducts was contrived. In this report, the GC/MS technique was shown to be applicable in identifying the nature of the trapped aryl radicals unambiguously. Moreover, it enables us to identify several coexisting radicals in the same run. Since spin trapping method is often applied to a complex radical-forming-reaction producing several diamagnetic by-products in






(4)

addition to spin adducts, mass chromatographic (MC) method is suitable for finding out the GC peaks of spin adducts.

In several cases, molecular ion peaks of spin adducts were observed directly. For example, the α-phenyl *N*-*t*-butyl nitrone (PBN, 1a) adduct of 2-cyano-2-propyl radical gave m/z $245(M^{+})$, $244[(M-1)^{+\cdot}]$, and $188[(M-C_4H_9)^{+\cdot}]$ peaks in its mass spectrum, from which the free radical could be identified unambiguously. In many other cases, spin adducts were so unstable that their mass spectra could not be observed by the direct measurement. Some of them tend to decompose even under the conditions for gas chromatographic separation. Therefore, spin adducts were trimethylsilylated on the nitroxyl oxygen atoms.4) The trimethylsilyl derivatives (3) are more stable and more volatile than the spin adducts themselves, being suitable for GC/MS measurements. The α-4-pyridyl 1-oxide *N*-*t*-butyl nitrone (1b) adduct of hydroxyl radical was bis-trimethylsilylated both on the nitroxyl and on the hydroxyl oxygen atoms giving 4. Its mass spectrum has m/z $356(M^{+\cdot})$, $355[(M-1)^{+}]$, and other fragment peaks(Table 1).

The PBN adducts of aryl radicals (3a)5) gave no molecular ion peaks even after trimethylsilylation. The $(M-58)^{+\cdot}$, $(M-73)^{+}$, and $(M-147)^{+}$ peaks are more intense than others and very characteristic of these compounds, being probably formed by the successive fragmentation given in the following scheme from the molecular ion. The compositions of the fragment peaks in the case of 5(X = H) were determined by measuring its high resolution spectrum. The $(M-73)^{+}$ peak was not assigned to the cation of

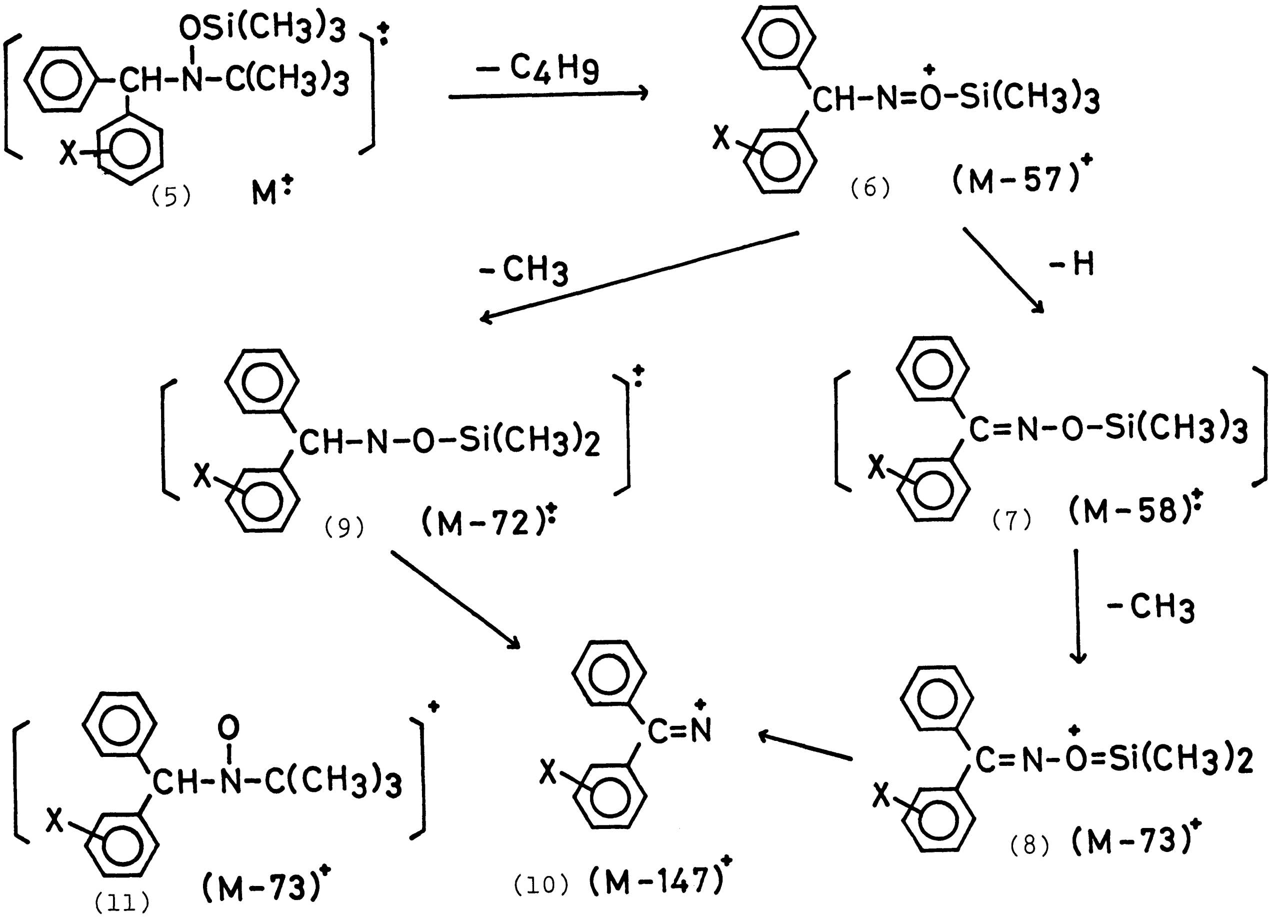


Table 1. GC/MS Spectra of Trimethylsilylated Spin Adducts[a]

Spin Adduct	Method[b]	M	t/min[c]	Relative Intensity (Base Peak =100)			
				$(M-58)^{+\cdot}$	$(M-73)^{+}$	$(M-147)^{+}$	
3a R:C_6H_5	A	327	7.7	35	15	100	
2-ClC_6H_4	B	361	8.0	33	31	100	
			8.4	30	31	100	
3-ClC_6H_4	B	361	9.0	45	40	100	
4-ClC_6H_4	A	361	9.4	12	13	100	
4-ClC_6H_4	B	361	9.3	26	13	100	
2-BrC_6H_4	B	405	9.3	21	20	100	
			9.8	14	15	100	
3-BrC_6H_4	B	405	9.2	29	19	100	
4-BrC_6H_4	B	405	9.7	28	18	98[d]	
2,6-$Cl_2C_6H_3$	B	395	9.8	31	37	100	
			10.4	18	26	100	
4-$CH_3C_6H_4$	A	341	6.6	36	12	100	
4-$NO_2C_6H_4$	A	372	9.2	14	24	100	
1-Naphthyl	B	377	9.2	30	4	100	
			9.8	26	4	100	
				$M^{+\cdot}$	$(M-1)^{+}$	$(M-57)^{+}$	$(M-131)^{+}$
4	C	356	18.1	9	25	67	100

a) A Shimadzu gas chromatograph-mass spectrometer Model LKB-9000B was used. The instrument was programmed to hold at 120°C for 1 min and to raise to 230°C at a linear increase of 20°C per minute using OV-17 column.
b) The free radical was formed by thermal decomposition of the corresponding arylazo-triphenylmethane (method A), by photolysis of the corresponding bromoarene (method B), or from sodium peroxodisulfate (method C).
c) t: retention time. d) The ^{81}Br isotope peak of $(M-147)^{+}$ is the most intense.

the spin adduct (11) generated by the elimination of trimethylsilyl(M = 73) moiety.[6)] When a substituent is present at the ortho position, two peaks were observed in the chromatogram (as indicated by the arrows in Fig. 1). Since their mass spectra were practically the same, the peaks might be assignable to isomeric species having very similar structures. As all of these peaks (given in Table 1) are dependent on the molecular weight of the parent spin adduct, they can be used to determine the nature and the relative amount of the trapped aryl radical even when more than one free radicals are present together. For example, a run in which a mixture of an equimolar amount of phenylazo- and *p*-bromophenylazo-triphenylmethanes was decomposed in the presence of PBN gave two GC peaks (t, 7.6 and 9.6 min; intensity ratio(uncorrected), 1.4) assignable to 3a's(R: C_6H_5 and *p*-BrC_6H_4) by MC measurement monitored by the same fragment ions as the measurements given in Table 1. The mass spectra corresponding to these peaks were nearly identical with those given in Table 1.

This method will provide a sure and widely applicable way to identify spin-trapped radicals when used together with ESR spectroscopy.

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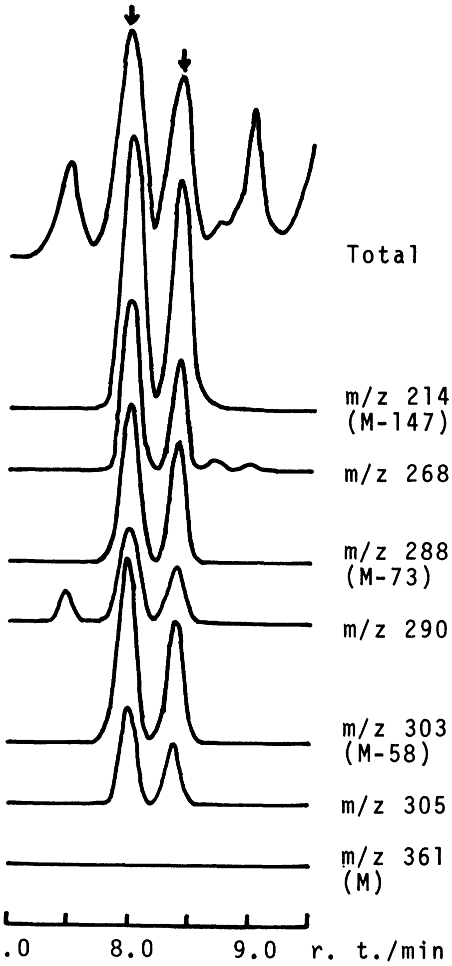

Fig. 1. Mass chromatogram of the trimethylsilylated PBN adduct of *o*-chlorophenyl radical.

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4) Trimethylsilylation was carried out with *N,O*-bis(trimethylsilyl)acetamide (in cases of the aryl radical adduct) or with hexamethyldisilazane (in the case of the hydroxyl radical adduct). See (a) D. F. Zinkel, B. M. Lathrop, and L. C. Zank, *J. Gas Chromatogr.*, 6, 158 (1968) and (b) S. Friedman and M. L. Kaufman, *Anal. Chem.*, 38, 144 (1966). The GC/MS measurement was carried out using the crude residue obtained after the evaporation of the solvent and the unreacted reagent in vacuo.

5) ESR spectra of 3a's were reported by M. Kamimori and co-workers [M. Kamimori, H. Sakuragi, T. Suehiro, K. Tokumaru, and M. Yoshida, *Bull. Chem. Soc. Jpn.*, 50, 1195 (1977)].

6) The (M-73)$^+$ is a single peak even under the conditions of high resolution measurement. Its observed mass is 254.0952 ± 0.0013; while the calculated masses for 8 and 11 are 254.1002 and 254.1546, respectively.

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