CHEMISTRY LETTERS, pp. 1935-1938, 1989.

Spin Distribution in the Phenyldiazenyl Radical

Tadashi SUEHIRO,* Toshiaki SATO, Tetsuya SANO, Akemi KOIKE,
and Anton RIEKER+
Department of Chemistry, Faculty of Science, Gakushuin University,
Mejiro, Toshimaku, Tokyo 171
+Institut für Organische Chemie der Universität Tübingen,
Auf der Morgenstelle 18, D-7400 Tübingen, Germany

Hyperfine coupling constants of carbons in the benzene ring of phenyldiazenyl radical were determined. The high hfs constant of C-1, 62.2 G, is a characteristic nature of phenyldiazenyl.

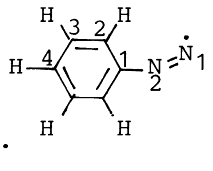
We have previously reported the detection of aryldiazenyl radicals by the ESR method in a steady state concentration at low temperatures.[1] Based on the experimental hfs constants of N and H by reference to the INDO calculations, we proposed a conformation of phenyldiazenyl with the N=N group, rotating about the C^1-N^2 bond axis. We describe here further results on ^{13}C hfs constants of the benzene ring of the radical.

In Table 1 the ^{13}C hfs constants of phenyldiazenyl radical are listed together with those of ^{14}N and ^{1}H,[1] in comparison with the hfs constants of phenyl radical.

Table 1. Hyperfine Coupling Constant of Phenyldiazenyl and Phenyl Radicals

Hfs const. / Position	Phenyldiazenyl[a] Found	Phenyldiazenyl[a] Calcd[1]	Phenyl Found	Phenyl Calcd (G)[b]
N-1	9.45[1]	5.26	-	-
-2	22.5	18.14	-	-
C-1	62.2	13.10	135.21[2]	151.3
-2	2.06	0.67	7.42	-4.8
-3	0.51	0.21	12.56	10.8
-4	0.10	0.48	1.27	-2.6
H-2	0.0[1]	0.65	17.4[3]	18.8
-3	1.20	0.76	5.9	6.1
-4	0.0	-0.23	1.9	3.9

a) The numbering of atoms in phenyldiazenyl radical is as follows:

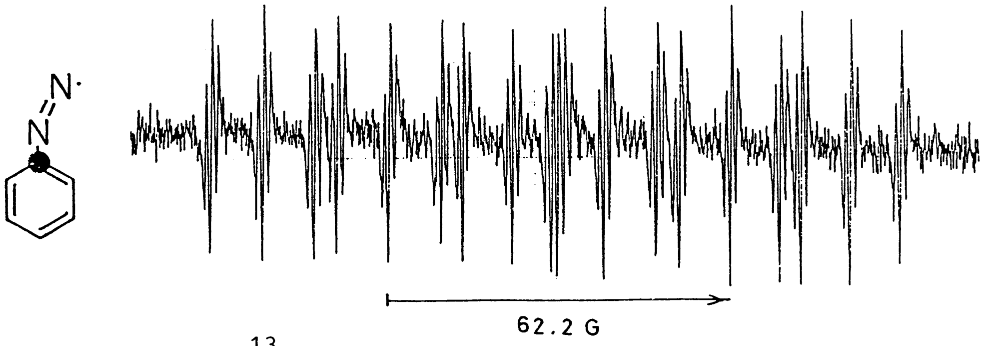


b) 1 G = 10^{-4} T

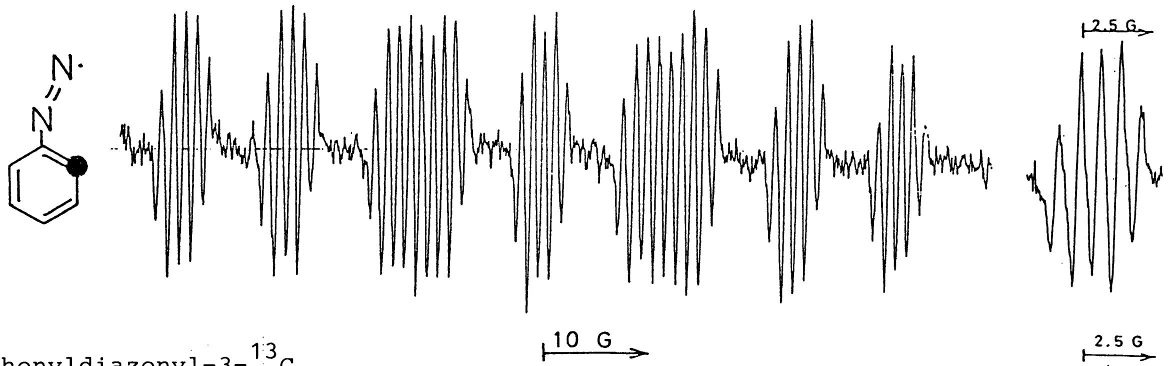
1, 2, 3) See the references in the text.

ESR spectra of ^{13}C-phenyldiazenyl radicals were reproduced in Fig. 1.

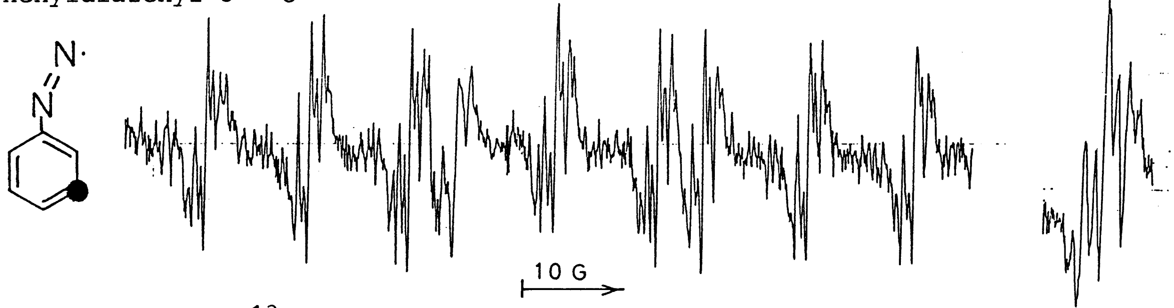
(a) Phenyldiazenyl-1-^{13}C



(b) Phenyldiazenyl-2-^{13}C



(c) Phenyldiazenyl-3-^{13}C



(d) Phenyldiazenyl-4-^{13}C

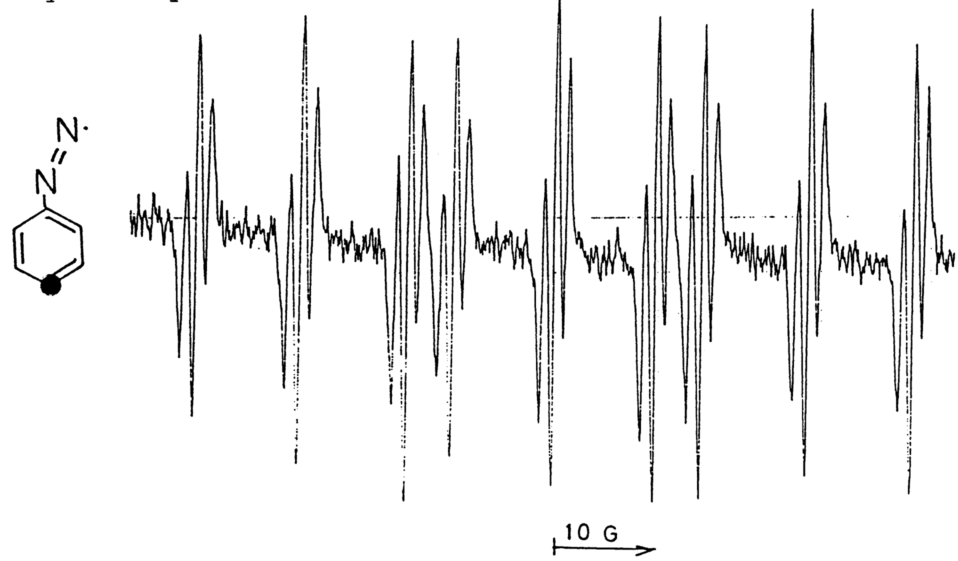


Fig. 1. ESR Spectra of phenyldiazenyls.

The hfs constant of ^{13}C-1 of phenyldiazenyl was high and near one half of that of phenyl radical.$^{2)}$ The experimental value was about 5 times as large as that calculated by the INDO method for the conformation of the minimum total energy, which gave a fair coincidence of N and H hfs constants with those of experiments.$^{1)}$ The dimensions used in the calculation were as follows: C^1-N^2 = 1.40 Å, N^2-N^1 = 1.20 Å, and angle C^1-N^2-N^1 = 140°.

The pattern of ^{13}C hfs constants of phenyldiazenyl was different from that of phenyl radical with respect to the alternation of spin densities of the latter radical: phenyldiazenyl showed spin densities decreasing strongly from the 1- to the 4-position. Although the INDO calculation reproduced the ESR results fairly well for phenyl radical (see Table 1), this does not so for phenyldiazenyl as was described above, and also not for the hfs constant of C-4. The calculations gave always higher values for C-4 than those for C-3, and this is contradictory to the experiment.

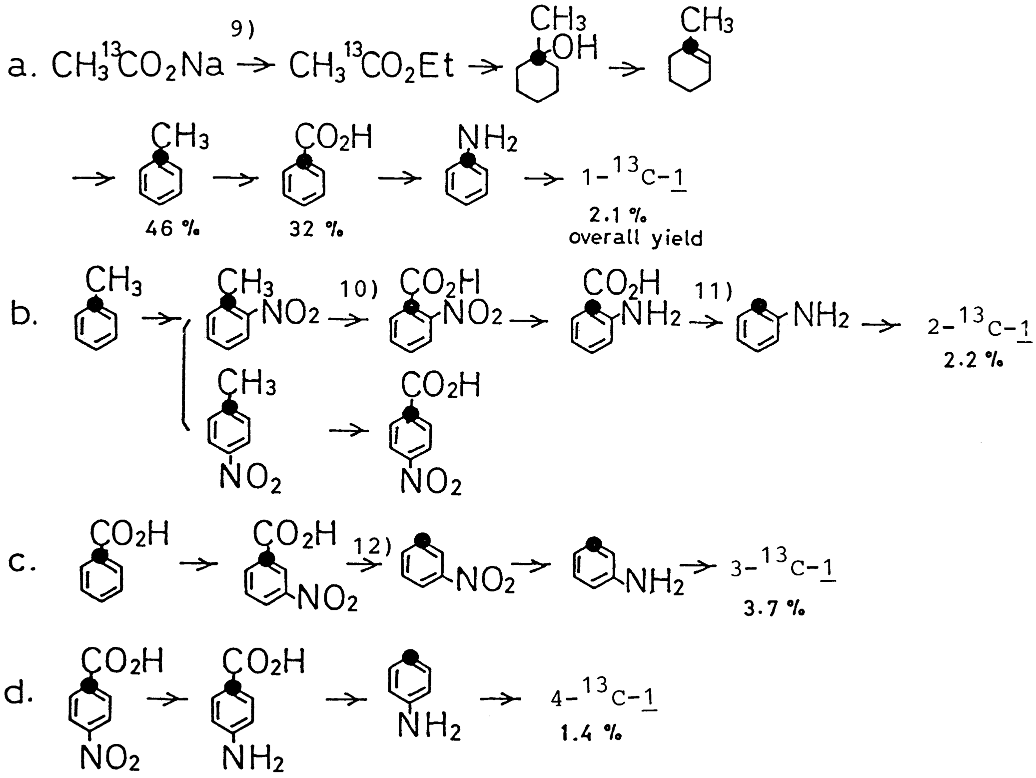
The optimized configuration of ethyldiazenyl radical by the MNDO method$^{4)}$ is similar to that of phenyldiazenyl by the INDO method$^{1)}$ in the group C^1-N^2-N^1: the bond length N^2-N^1 in ethyldiazenyl, 1.15 Å, is close to 1.20 Å in phenyldiazenyl and the angle C^1-N^2-N^1, 133°, close to 140°, although the bond length C^1-N^2, 1.53 Å, differs from 1.40 Å, caused by the change of orbital from sp^3 to sp^2. The spin density in 2s of C^1 calculated for ethyldiazenyl$^{4)}$ is ca. one third of that of N^2 and this is also the case for phenyldiazenyl in the INDO method.$^{1)}$ The high hfs constant of C^1 of diazenyl radical is not compatible with these optimized configurations.

The spin distribution in phenyldiazenyl was very different from that of benzoyloxyl radical.$^{5)}$ The ^{13}C-carbonyl of benzoyloxyl exhibited a hfs constant of 13.3 G and the most of the spin density of the radical was localized in 2p orbitals of both oxygens. The hfs constant of C-1 of the benzene ring can be assumed to be small, because ^{13}C-1 and ^{13}C-2 of 4,4-dimethyl-2-pentynoyloxyl radical afforded 13.3 and 4.92 G, respectively.$^{6)}$

Benzoyl radicals are similar to phenyldiazenyl radicals, except for the high hfs constant of carbonyl-^{13}C, 128.7 G.$^{7)}$ The hfs constant of C-1 of the benzene ring is presumable about 42 G, one third of that of carbonyl, referring to the result on carboxymethylformyl radical, $HOOCCH_2\dot{C}{=}O$.$^{8)}$

The high value of 62.2 G of C-1 of phenyldiazenyl radical corresponds to 7.6% spin density in s-orbital of carbon and it is higher than 5.6% spin density of the neighboring nitrogen. This is a characteristic feature of phenyldiazenyl radical.

The starting compounds for the ESR measurement of phenyldiazenyls, phenyl(4-t-butylphenylthio)diazenes, (1), carrying ^{13}C in the required position in the benzene ring, were prepared from sodium acetate-1-^{13}C (^{13}C, 99%), according to the standard methods as illustrated in the Scheme 1. The position of ^{13}C in the labelled anilines was confirmed by ^{13}C-NMR. The measurement of ESR was performed as described before.$^{1)}$



Scheme 1. Preparation of phenyl(4-t-butylphenylthio)diazenes (1)

References

1) T. Suehiro, S. Masuda, T. Tashiro, R. Nakausa, M. Taguchi, A. Koike, and Anton Rieker, Bull. Chem. Soc. Jpn., 59, 1877 (1986); T. Suehiro, T. Tashiro, and R. Nakausa, Chem. Lett., 1980, 1339.
2) H. Zemel and W. Fessenden, J. Phys. Chem., 79, 1419 (1975).
3) P. H. Kasai, E. Hedeya, and E. B. Whipple, J. Am. Chem. Soc., 91, 4364 (1969).
4) J. J. Dannenberg and D. Rocklin, J. Org. Chem., 47, 4529 (1982).
5) R. A. Merril, PhD Thesis of Yale University 1981, Diss. Abstr., B 47, 3372 (1987), cited in Ref. 6.
6) H. G. Korth, J. Chateauneuf, J. Lusztyk, and K. U. Ingold, J. Am. Chem. Soc., 110, 5929 (1988).
7) P. J. Krusic and T. A. Rettig, J. Am. Chem. Soc., 92, 722 (1970).
8) R. C. McCally and A. L. Kwiram, J. Am. Chem. Soc., 92, 1441 (1970).
9) M. Fields, M. A. Leaffer, S. Rothchild, and J. Rohan, J. Am. Chem. Soc., 74, 5498 (1952).
10) L. Vanino, Präp. Chem. II Bd., Org. Teil, p.569. Separation of m-nitrobenzoic acid as Ba salt from the ortho isomer.
11) L. McMaster and R. L. Shriner, J. Am. Chem. Soc., 45, 751 (1923).
12) T. Cohen, R. W. Berninger, and J. T. Wood, J. Org. Chem., 43, 837 (1978).

(Received July 28, 1989)