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SPIN TRAPPING REACTION OF DIMERIC NITROSOARENES. POSSIBLE FORMATION OF NITROXIDE RADICAL OF TRIAZACYCLOPROPANE STRUCTURE

Tadashi SUEHIRO, Seiichi MASUDA, and Nobuyuki MOTOYAMA

Chemistry Department, Faculty of Sciences, Gakushuin University
Toshimaku, Mejiro, Tokyo 171

o-Disubstituted nitrosoarenes such as 2,6-dimethyl-, 2,4,6-trimethyl-, and 2,3,5,6-tetramethyl-nitrosobenzenes trap free radicals not only in their monomeric but also in dimeric forms. Diphenylmethyleneamino radicals thus add to nitrosoarene dimer in preference to monomer to yield nitroxides containing possibly triazacyclopropane structure.

2,3,5,6-Tetramethylnitrosobenzene (Nitrosodurene, ND) is one of the excellent spin trapping agents and when monomeric ND captures free radical, it shows ESR spectrum which is not affected by hydrogen atoms on the durene moiety.[1)]

On heating a solution of 1.54 mg ND and 1.30 mg bis(diphenylmethylenecarbamoyl) peroxide[2)] in 1 ml CCl_4 at 40 - 50 °C for a short time, we obtain an ESR spectrum of quintet (1:2:3:2:1) of triplets (1:1:1) (Fig. 1,Run 1 of the Table). From the findings described below, it was concluded that the spectrum came from a nitroxide I shown in Fig. 2, which was derived from dimeric ND and an iminyl radical.

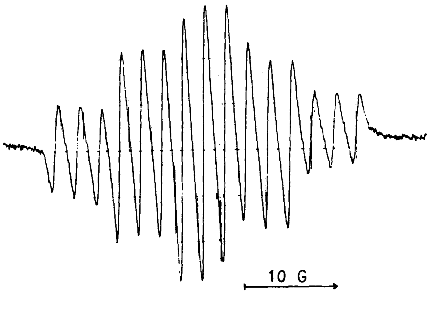

Fig. 1

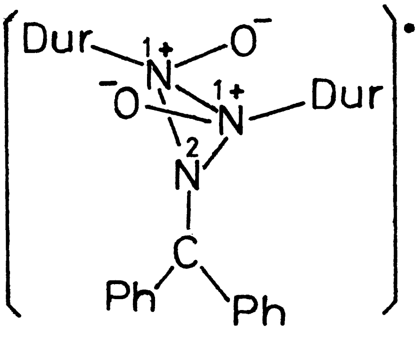

Fig. 2

To elucidate the structure of the nitroxide I, ESR experiments were performed using ^2H or ^{15}N labeled ND, ^{15}N labeled peroxide, and also using

2,6-dimethyl- and 2,4,6-trimethyl-nitrosobenzenes. The results are listed in the Table.

Table. ESR-SPECTRA OF NITROXIDES FORMED BY THE REACTION BETWEEN NITROSOARENE AND BIS(DIPHENYLMETHYLENECARBAMOYL) PEROXIDE

Run	N^1	N^2	g	hfs, Multiplicity $2\cdot N^1$, a_N1 (gauss)	hfs, Multiplicity N^2, a_N2 (gauss)
1	ND	Iminyl	2.0061	5 (1:2:3:2:1) 6.9_8	3 (1:1:1) 2.2_5
2	ND	Iminyl-^{15}N	2.0060	5 (1:2:3:2:1) 7.0_7	2 (1:1)*) 3.3_0
3	ND-^{15}N	Iminyl	2.0061	3 (1:2:1) 9.6_5	3 (1:1:1)**) 2.3_8
4	ND-^{15}N	Iminyl-^{15}N	2.0060	3 (1:2:1) 9.9	2 (1:1) 3.5
5	ND-^2H	Iminyl	2.0061	5 (1:2:3:2:1) the same as Run 1	3 (1:1:1)
6	2,4,6-Trimethyl-nitrosobenzene	Iminyl	2.0060	5 (1:2:3:2:1) 6.9_5	3 (1:1:1) 2.5_0
7	2,6-Dimethyl-nitrosobenzene	Iminyl	2.0061	5 (1:2:3:2:1) 6.9_5	3 (1:1:1) 2.4_5

Iminyl stands for $Ph_2C{=}N\cdot$ radical.
*) The spectrum is shown in Fig. 3.
**) The spectrum is shown in Fig. 4.

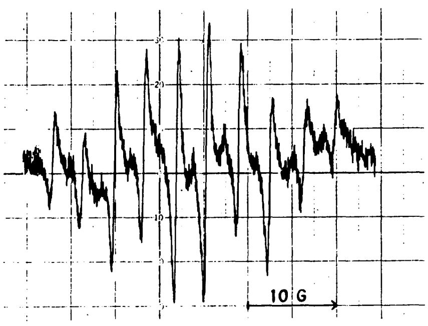

Fig. 3

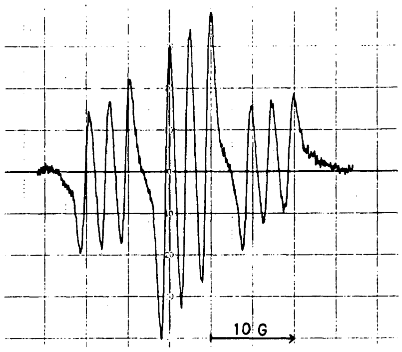

Fig. 4

The g values of the radicals listed in the Table accord well with that of the usual nitroxides1) and the spectra are best explained using the model I;

the nitroxides are composed of two equivalent nitrogen atoms derived from two molecules of ND (N^1 of the Table) and one another kind of nitrogen from the iminyl radical (N^2 of the Table). Hydrogens on nitrosoarene have no effect on ESR spectra (Runs 1,5,6,7).

The two equivalent nitrogen atoms from nitrosoarenes of coupling constant ca. 7 gauss suggest a N-N bond in the nitroxide of structure O-$\overset{|}{\text{N}}$-$\overset{|}{\text{N}}$-O· Alkyl duryl nitroxides are, however, too stable to add to another molecule of ND. It is therefore very plausible to assume that the nitroxide I was formed by addition of iminyl radical to dimeric ND. 2,6-Dimethyl- and 2,4,6-trimethyl-nitrosobenzenes can also give in this manner nitroxides of the structure I, because dimeric nitrosoarenes are present in solution in an appreciable concentration.

ND,[3] 2,4,6-trimethylnitrosobenzene,[4] and 2,6-dimethylnitrosobenzene[5] are known to be in equilibrium in solution between monomeric and dimeric forms. The equilibrium constant for dimerization (M^{-1}) of ND in CCl_4 was determined to be 1030 at 30 °C and 604 at 39 °C. Dimeric ND in CCl_4 is present in sufficiently high concentration to spin-trapping in solution. The configuration of the dimer in CCl_4 is probably trans (IR; 1270 cm^{-1}).[6]

The method of INDO calculation was applied to estimate the most stable geometry of the nitroxide I, and to find whether the calculation yields two equivalent a_N1 values which are larger than a_N2. INDO calculations, putting H in place of Dur and Ph of the nitroxide I and of other open chain nitroxide Dur-$N(O\cdot)$-$N^+(O^-)$(Dur)-$N{=}CPh_2$, have lead to the most stable nitroxide having triazacyclopropane structure and the geometry was given as follows: $r_{N^1-N^1}$ = 1.42 Å, $r_{N^1-N^2}$ = 1.37 Å, the angle O-N^1-Dur = 116°, and the angle between the axis N^1-N^1 and the plane O-N^1-Dur = 16°, with a_N1 = 38 gauss and a_N2 = 1.6 gauss. The calculations showed also that for the open chain nitroxide the a_N value of nitrogen N^1 adjacent to nitroxide nitrogen is different from that of a_N value of nitroxide nitrogen. Based on these calculations a nitroxide of cyclic structure like I is conceivable. An open chain nitroxide, in which the interchange of the N^1-N^2 bond formation is very fast (half life of each conformer is less than 10^{-10} s), is also acceptable to explain the experimental results. This model can not be, however, distinguished from the cyclic non-classical formulation by the technique at hand, and we propose the latter formulation here.

The hyper fine coupling constants of the Table do not change in the range of temperature from -10 °C to +50 °C and in the range of solvent from CCl_4 to toluene. And the nitroxide I is more stable in CCl_4 at room temperatures than in benzene or in toluene; in the latter solvents it is necessary to keep the ESR cavity at low temperatures for the measurements.

In the formation of the nitroxide I, the low energy level of the $N^+ = N^+$ double bond of nitrosoarene dimer must play an important role, because the iminyl radical is electronegative and because the iminyl radical will be promoted from π-radical to σ-radical during the course of the reaction.[7] The addition reaction of the iminyl radical should be aided by the interaction between p-orbital occupied of the iminyl and the π^*- orbital of $N^+ = N^+$ bond together with the interaction between sp-orbital, singly occupied, of the iminyl and the π-orbital of $N^+ = N^+$ bond.

References and Notes

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5) 2,6-Dimethylnitrosobenzene is present more than 50% in dimeric form in a cold benzene solution. E. Bamberger and A. Rising, Ber., 34, 3877 (1901).
6) No IR bands indicating cis configuration were found in the range 1380 - 1410 cm^{-1}.
7) A. J. Lawson, J. Chem. Soc. Chem. Commun., (1974) 488.

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