CHEMISTRY LETTERS, pp. 985-988, 1980.

HYPERFINE SPLITTING CONSTANTS OF BIS(2,6-DIMETHYLARYL) NITROXIDES

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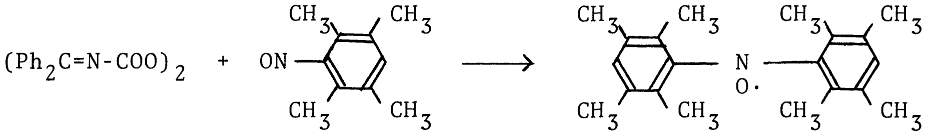
Bis(2,6-dimethylaryl) nitroxides showed ESR spectra of complex hyperfine structures and the coupling constants of the ring and the methyl hydrogen atoms were determined by a simulation technique. The coupling constants of the 4-ring and the 4-methyl hydrogen atoms of the aryl group, ca. 1.1 gauss, suggest a fairly great degree of conjugation between the aryl and the nitroxide group.

2,3,5,6-Tetramethylnitrosobenzene (1) (nitrosodurene) is a spin trapping agent widely used because the nitroxide derived from 1 shows ESR spectra, whose hyperfine structures are due to the hydrogen atoms carried only on the trapped radical.[1)] The fact that the ESR spectra are not fine splitted by the hydrogen atoms of the duryl moiety of the nitroxide can be explained supposing a complete cross of conjugation between the duryl and the nitroxide groups, so that a very small spin density of the nitroxide is distributed through sigma bonds in the 4-ring hydrogen of the duryl group (ca. 0.3 gauss or less). The similar cross of conjugation has been proposed for t-butyl 2,6-disubstituted aryl nitroxides.[2)] We found however a fairly great degree of conjugation between the duryl and the nitroxide group in diduryl nitroxide.

By the reaction between 1 and bis(diphenylmethylenecarbamoyl) peroxide (5) in benzene in an Ar atmosphere at 60 - 70 °C, we observed ESR signals of a triplet of multiplets (Ia) of more than 33 fine lines (Fig. 1). That the hydrogen atoms of nitrosodurene contribute to the fine structure of Ia was demonstrated by the experiment using perdeuterionitrosodurene (d-1): by the reaction between d-1 and 5 an ESR spectrum composed of three broad lines, $g = 2.006_2$ and $a_N = 10.38$ gauss, was observed. To determine the structure of the nitroxide which gave an ESR signal Ia, we examined the ESR spectra of nitroxides derived from several 2,6-dimethylnitrosoarenes, ^{15}N-labelled nitrosoarenes, and ^{15}N-labelled peroxide 5, and we came to the conclusion that the nitroxide which gave Ia was diduryl nitroxide.

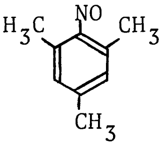


5 1

Reactions of 5 with 2, 3, and 4 gave nitroxides which showed ESR signals IIa, IIIa, and IVa, respectively. Their g-values range from 2.006_1 to 2.006_3. The multiplet of IVa was the simplest, nevertheless having more than 13 lines.

The reactions between ^{15}N-4 and 5, 4 and ^{15}N-5, and ^{15}N-4 and ^{15}N-5, all showed ESR spectra of the same hyperfine structure of more than 13 lines except that ^{15}N-4 induced an alternation from a triplet, $a_{^{14}N}=10.2_3$ gauss to a doublet, $a_{^{15}N}=14.5_5$ gauss. The nitrogen of 4 was incorporated in the nitroxide only in the nitroxide-nitrogen, and the nitrogen atom of 5 was not incorporated. The best simulation of IVa was obtained as that of bis(2,6-dimethyl-4-t-butylphenyl) nitroxide, as shown in Fig. 4, IVa'.

The conclusion drawn from the spectral simulation described above was confirmed experimentally by the reaction between 1 and durylmagnesium bromide in tetrahydrofuran at -45 - -15 °C, followed by oxidation. It gave a nitroxide whose ESR signal Ie coincided very well with Ia.



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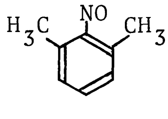

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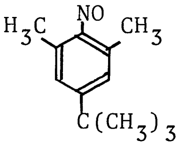

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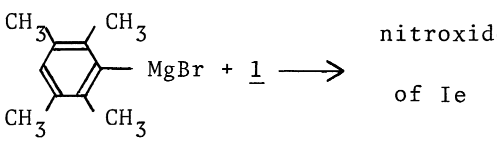
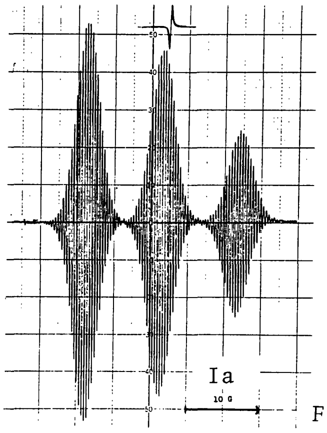
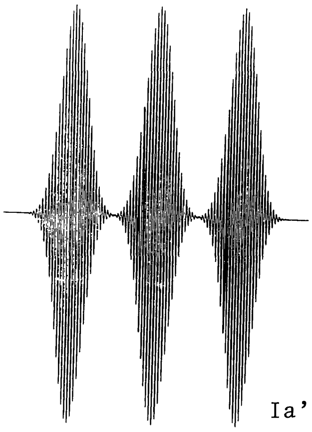


The ESR spectra Ia, IIa, and IIIa were also simulated successfully as those of bis(2,6-dimethylaryl) nitroxides, respectively as shown in Fig. 1, Ia', Fig. 2, IIa', and Fig. 3, IIIa'. The hyperfine coupling constants of hydrogen atoms so determined for Ia - IVa are listed in the Table. They can be summarized as follows: a) the 2- and the 6-methyl hydrogen atoms have coupling constants 0.7 - 0.8 gauss, b) the ring hydrogen atoms in the 3- and the 5-positions have a-values 0.74 - 0.78 gauss, c) the 3- and the 5-methyl hydrogen atoms have a-values ca. 0.36 gauss, and d) the 4-ring and the 4-methyl hydrogen atoms have coupling constants 1.1 - 1.2 gauss.

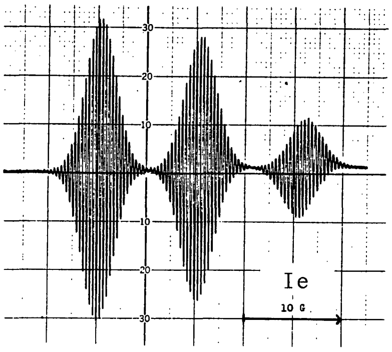


Ia

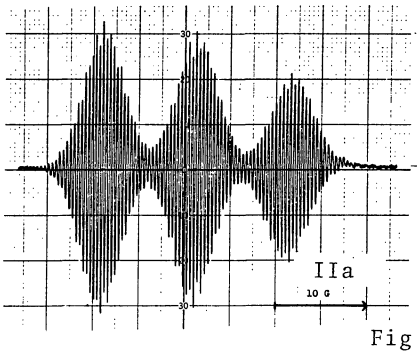
Fig. 1



Ia'

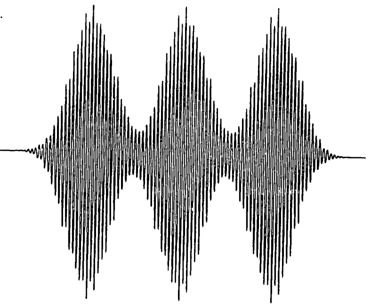


Ie



IIa

Fig. 2



IIa'

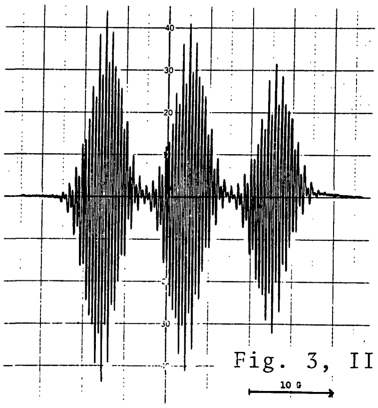


Fig. 3, IIIa

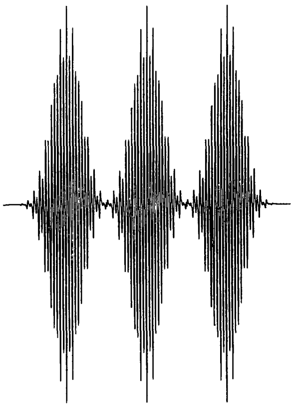
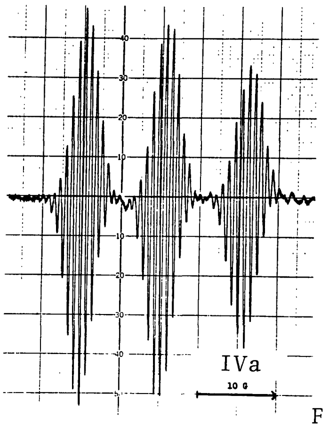
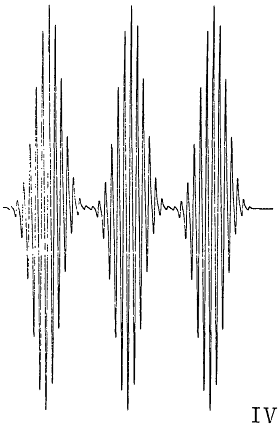


Fig. 3, IIIa'



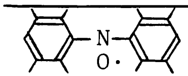
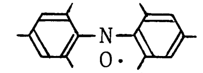
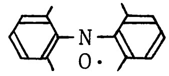
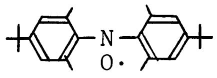
IVa

Fig. 4



IVa'

Table. HYPERFINE COUPLING CONSTANTS OF BIS(2,6-DIMETHYLARYL) NITROXIDES DETERMINED BY SPECTRAL SIMULATION(gauss)

Nitroxide	ESR spectrum	g	a_N	$a_{2\text{-}CH_3}$	$a_{3\text{-}H}$	$a_{3\text{-}CH_3}$	$a_{4\text{-}H}$	$a_{4\text{-}CH_3}$
	Ia	2.006_2	10.25	0.72		0.36	1.08	
	IIa	2.006_2	10.14	0.82	0.74			1.24
	IIIa	2.006_3	10.30	0.78	0.78		1.17	
	IVa	2.006_1	10.23	0.78	0.78			
t-butyl 2,6-dimethoxyphenyl nitroxide[2b)]			13.3		0.69		0.1-0.2	$(^{a_{t\text{-}Bu}}_{0.33})$

The coupling constants of the 3-ring hydrogen atoms accord with that of diphenyl nitroxide, ca. 0.8 gauss,[3)] and also with that of t-butyl 2,6-dimethoxyphenyl nitroxide,[2b)]in the latter case the aromatic ring is probably tilted from the plane O-N-C(aromatic) to about 90°. The coupling constants of the 4-ring and the 4-methyl hydrogen of Ia - IIIa, 1.1 - 1.2 gauss, are however much larger than that of t-butyl 2,6-disubstituted phenyl nitroxide, ca. 0.2 gauss,[2)] but by far smaller than that of diphenyl nitroxide, 1.97 gauss.[3)] In diphenyl nitroxide a conjugation among the phenyl rings and the nitroxide group is assumed. These results suggest that in bis(2,6-dimethylaryl) nitroxides the 2,6-dimethylaryl groups conjugate fairy well to the nitroxide group,eventhough the two aryl groups are probably lying perpendicular to each other.

A possible mechanism for the formation of diaryl nitroxide by the reaction between nitrosoarene and bis(diphenylmethylenecarbamoyl) peroxide will be reported in the next communication.

References

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2) a) A. Calder, A. R. Forrester, J. W. Emstet, G. R. Luckhurst, and R. A. Storey, Mol. Phys., 18, 481 (1970); b) H. J. Jakobsen and K. Torssell, Tetrahedron Lett., 1970, 5003.

3) J. R. Thomas, J. Am. Chem. Soc., 82, 5955 (1960).

(Received April 14, 1980)