Tetrahedron Letters No.57, pp.5003-5006, 1970. Pergamon Press. Printed in Great Britain.

ESR AND NMR SPECTRA OF THE 2,6-DIMETHOXYPHENYL-<u>t</u>-BUTYLNITROXIDE RADICAL. EXPERIMENTAL DETERMINATION OF COUPLING PARAMETERS BY INDEPENDENT METHODS

H.J. Jakobsen and Kurt Torssell* Department of Organic Chemistry, University of Aarhus 8000 Aarhus C, Denmark

(Received in UK 2 November 1970; accepted for publication 13 November 1970)

In view of recent results from NMR and ESR investigations on sterically hindered ary 1 <u>t</u>-butylnitroxides, 1, 2 the data reported³ for 2,6-dimethoxyphenylt-butylnitroxide, Ia, seemed to be doubtful. The spectrum of Ia, that was generated in situ in the ESR cavity from 2,6-dimethoxyiodobenzene as previously described, 4 differed from that reported, but resembled closely those of other 2,6-disubstituted aryl t-butylnitroxides.² A common feature in the ESR spectra of these sterically hindered radicals is that the t-butyl protons give rise to a hyperfine splitting of about 0.3-0.4 gauss, complicating the analysis considerably. In radicals, where the nitroxide group is freely rotating, the observation of this hyperfine splitting (~0.1 gauss) is usually limited by the resolution of the instrument. In the ortho-disubstituted radicals the meta-protons have a coupling constant of about 0.7 gauss, i.e., twice the t-butyl proton coupling, whereas the coupling arising from the para-proton is much smaller $(\sim 0.1 \text{ gauss})$ and generally has a line-width broadening effect only. The spin distribution in the ring is thus completely different from that in the sterically unhindered series: a_0 : a_m : $a_p \sim 2:1:2$. This also stands in sharp contrast to the situation in nitro-aromatic anions, where the spin density decreases more or less uniformly in the ring, when the nitro group is rotated out of conjugation by steric hindrance.⁵ The reasons for these effects are still obscure. One should expect a basic 3 x 14 line spectrum of Ia and this was actually obtained. Furthermore, the use of deuterated <u>t</u>-nitrosobutane² as scavenger simplified the spectrum to a 3 x 3 line spectrum (Figure 1, Ib) from which

the <u>meta</u>-proton coupling constant was determined. A secondary doublet splitting of ~0.1-0.2 gauss emanating from the <u>para</u>-proton could also be observed at low radical concentrations.



The experimental data are collected in Table 1. However, the coupling constants do not agree with the earlier reported values calculated from NMR contact shifts.³ Ia was therefore synthesized⁶ and the ¹H NMR spectrum recorded at 100 MHz on a Varian HA-100 spectrometer, operating in the HR-mode with a modulation frequency of 13 KHz (Figure 2). NMR spectra of radicals are characterized

TABLE 1. Contact Shifts^a and Hyperfine Splitting Constants obtained for the Radicals Ia and Ib, $a_N = 13.3$ gauss

Protons	Inten- sity	Line position from TMS (Hz), Ia	Shift (ΔH) from hydroxylamine ^b (Hz)	Line width (Hz), Ia	Calc.hfs. (gauss) Ia	hfs, from ESR(gauss), Ia and Ib
р-н	1	-567	+1267	210	-0.17	0.1-0.2
<u>m</u> -H	2	+6014	-5314	825	+0.71	0.69
<u>t</u> -Butyl	9	-2216	+2326	630	-0.31	0.33
OCH ₃	6	+670	-292	220	+0.04	· ·

^aIn Hz at 100 MHz.

^bCalculated using the chemical shift data of Ref.3 for the corresponding hydroxylamine.

by very broad signals with a line width at half peak height of several hundred Hz and extraordinary large shifts, the direction and magnitude of which allow a determination of signs and magnitudes of the hyperfine coupling constants, eqn. (1).7

$$a_{H_{\underline{1}}} = -3.73 \ \Delta H_{\underline{1}} \times 10^4 \ Hz \ (T = 295^{\circ} K) \tag{1}$$

 $\Delta H_{\underline{i}}$ is the shift (positive in the upfield direction) in ppm for a magnetic nucleus \underline{i} with reference to its position in a related diamagnetic compound.



FIG.1. ESR Spectrum of Ib. The peaks marked "a" denoted the Spectrum of di-<u>t</u>-butyl d_g nitroxide.



FIG.2. NMR Spectrum of Ia in $CDCl_3$ (ca. 40% w/w).

In the NMR spectrum of Ia the presence of a broad signal from the <u>meta</u> protons was detected at +6014 Hz (relative to internal TMS), a signal which was not observed by Kreilick.³ Furthermore, from the ESR spectra of Ia and Ib the NMR assignments of Kreilick were shown to be in error. The values resulting from the NMR and ESR spectra of the present investigation agree within the limit of experimental error.

A point of interest is that the peak for the <u>ortho</u>-methoxy protons is shifted downfield like an <u>ortho</u>-methyl group, <u>i.e</u>. the unpaired spin density on the ring carbon leaks out on the oxygen with conservation of its sign. The assignment of the NMR absorption at +670 Hz (from TMS) to the methoxy protons, <u>i.e.</u>, $a_{OCH_3}^0 = +0.04$ gauss is supported by our finding that the peak for the methoxy protons of bis-(<u>p</u>-methoxyphenyl)-nitroxide is shifted downfield in its NMR spectrum, $a_{OCH_3}^p = +0.21$ gauss. This agrees almost too well with the value of 0.21 gauss determined by ESR measurements,⁶

<u>Acknowledgement</u>. We thank Dr. K. Schaumburg, University of Copenhagen, for technical assistance in recording the NMR spectra. This work was supported by a grant from <u>Danish Natural Science Research Council</u>.

REFERENCES

- Calder, A., Forrester, A.R., Emsley, J.W., Luckhurst, G.R., and Storey, R.A. <u>Mol.Phys.</u> <u>18</u>, 481 (1970).
- 2. Pedersen, J.A. and Torssell, K. To be published.
- 3. Kreilick, R.W. J.Chem. Phys. 45, 1922 (1966).
- 4. Torssell, K. Tetrahedron 26, 2759 (1970).
- 5. Geske, D.H. and Ragle, J.L. J.Am. Chem. Soc. 83, 3532 (1961).
- 6. Hoffman, A., Feldman, A.M., and Gelblum, E. J.Am.Chem.Soc. 86, 646 (1964).
- 7. McConnel, H.M. and Chesnut, D.B. <u>J.Chem.Phys</u>. <u>28</u>, 107 (1958).
- 8. Fischer, P.H.H. and Neugebaur, F.A. Z.Naturforsch. 21b, 1036 (1966).