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ELECTRON SPIN RESONANCE INVESTIGATION OF THE PHOTOLYSIS OF TERT-BUTYLNITROBENZENES AND (TRIMETHYLSILYL)NITROBENZENES

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SUMMARY

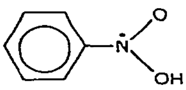
The photolysis of isomeric (trimethylsilyl)nitrobenzenes and of tert-butylnitrobenzenes produces arylalkoxynitroxide radicals which have been studied by ESR spectroscopy. Relative values of a_N suggest that the *p*-trimethylsilyl group exerts an overall withdrawing effect while the *m*-trimethylsilyl group has the opposite effect. The value of a_N for the *o*-trimethylsilyl radical indicates that steric interaction with the nitro group is probably minimal. *o*-(Trimethylsilyl)nitrobenzene free radical anion has been prepared; its a_N value suggests that steric interaction between groups on the aryl ring is also small in this case.

INTRODUCTION

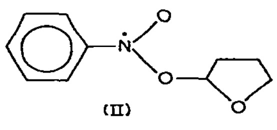
The role played by *d*-orbitals in *d*–π and *d*–π* interactions is of great interest[1] in fourth main-group organometallic chemistry. Convincing evidence of this type of conjugation has been adduced[2] from ESR studies of metal-containing aromatic radical anions and, to a lesser extent, of neutral free radicals. Other evidence has been obtained from a ^{14}N NMR investigation[3] of (trimethylsilyl)nitrobenzenes.

The production of neutral free radicals by the ultraviolet photolysis of nitrobenzenes was first reported by Ward[4]: we have suggested recently[5] that structure (II), rather than the previously accepted[6,7] structure (I), is more likely for the longest-lived radical produced by the photolysis of nitrobenzene in tetrahydrofuran (THF).

In order to obtain further evidence concerning metal–π* interactions, we have obtained ESR spectra of neutral arylalkoxynitroxide radicals formed by the photolysis of *o*-, *m*- and *p*-tert-butylnitrobenzenes in THF and also of their organosilicon analogues.



(I)



(II)

EXPERIMENTAL

o-, *m*- and *p*-tert-Butylnitrobenzenes were prepared[8] by direct nitration of tert-butylbenzene; the isomers were separated by preparative-scale gas–liquid chromatography. *o*-, *m*- and *p*-(Trimethylsilyl)nitrobenzenes were kindly donated by Professor J. C. Maire of Marseille University.

Solutions of the substituted nitrobenzenes ($\sim 0.1\ M$) in THF were deoxygenated by bubbling through nitrogen gas for ten minutes. Photolysis of a solution contained in a quartz aqueous sample cell was carried out in the cavity of a Varian V-4500 ESR spectrometer. Radiation was provided from the internal element of a 125 watt Osram type MB/U lamp, enclosed in an evacuated quartz jacket. The light was filtered with a piece of plane borosilicate glass in order to exclude wavelengths of less than 300 nanometres. The spectrometer was operated at X-band frequencies and the magnet field sweep was calibrated in two ways using (*i*) a sample of the naphthalene free radical anion[9] ($a_{H_\alpha} = 0.485$ millitesla) in 1,2-dimethoxyethane containing potassium and (*ii*) the radical obtained by ultraviolet photolysis of 2,3,5,6-tetrachloronitrobenzene[5] ($a_N = 2.500$ millitesla) in THF.

RESULTS AND DISCUSSION

The hyperfine splittings and line width parameters observed are listed in the Table. Hyperfine splittings were assigned by using a knowledge of the spin distributions in benzene-like radicals possessing a single strongly electron-withdrawing substituent, the unpaired electron being in the lowest anti-bonding orbital[10].

A significant feature in the results is the lower value of a_N for the *p*-$SiMe_3$ substituted radical (1.492 mT) compared with the organic analogue (1.548 mT). Decreased spin density at the nitrogen atom is an indication of an overall electron-withdrawing effect by the silicon atom, hence *d*-orbitals may be participating in bonding. However, confirmatory evidence from hyperfine coupling of the methyl group hydrogens was not obtained because of the small magnitudes of such coupling constants.

The reverse trend for the *m*-isomers ($a_N = 1.525$ mT for $SiMe_3$ and $a_N = 1.506$ mT for CMe_3) might indicate that conjugation is less effective for this configuration,

TABLE 1

ESR HYPERFINE SPLITTINGS[a] AND LINEWIDTHS[a] OF RADICALS FORMED BY PHOTOLYSIS OF TERT-BUTYL AND TRIMETHYLSILYL DERIVATIVES OF NITROBENZENE

Substituent	Line-width[b]	a_N[d]	a_{H_2}	a_{H_3}	a_{H_4}	a_{H_5}	a_{H_6}	$a_{H_{THF}}$
2-$SiMe_3$	0.059	1.494 ± 0.023		0.106	0.299	0.106	0.299	[c]
3-$SiMe_3$	0.024	1.525 ± 0.011	0.306		0.306	0.104	0.306	0.024
4-$SiMe_3$	0.039	1.492 ± 0.017	0.304	0.103		0.103	0.304	0.027
2-CMe_3	[e]	[e]	[e]	[e]	[e]	[e]	[e]	[e]
3-CMe_3	0.062	1.506 ± 0.003	0.302		0.302	0.106	0.302	[c]
4-CMe_3	0.057	1.548 ± 0.028	0.300	0.106		0.106	0.300	[c]

[a] In millitesla. [b] Peak to peak distance in first-derivative spectra. [c] The width of the lines was too large for a measurement to be made. [d] Standard deviations are quoted only for those values relevant to this paper. [e] See text.

and that the slightly higher value of a_N for the silicon compound is a result of induction by the trimethylsilyl group. It should be borne in mind that any conclusions must be tentative since these a_N values are almost within experimental error of each other. Interestingly, this work parallels that of Kazakova *et al.*[11] who prepared free radical anions from *m*- and *p*-(trimethylsilyl)nitrobenzenes (a_N equal to 1.07 and 0.98 mT respectively) by reduction with potassium in 1,2-dimethoxyethane.

Both electronic and steric effects may be important in determining the ESR spectra of radicals derived from the two *o*-compounds. Abundant evidence exists[12,13] for the out-of-plane twisting of nitro groups in *o*-substituted nitrobenzene anion free radicals: in related neutral arylalkoxynitroxide radicals this steric effect results[5] in increased spin density at the nitrogen atom with a consequent increase in a_N relative to the unhindered analogues. The magnitude of a_N for the *o*-SiMe$_3$ radical (=1.494 mT) is very similar to that for the unsubstituted radical[5] (=1.506 mT) and to that for the *p*-SiMe$_3$ radical. Since both induction and steric interaction with the nitro group are expected to increase a_N it can be concluded tentatively that any steric effect must be minimal. This conclusion conflicts with that of Vignollet, Maire and Witanowski[3] who invoked a steric effect to explain very small differences in ^{14}N chemical shifts of *o*-, *m*- and *p*-(trimethylsilyl)nitrobenzenes. Unfortunately, a direct comparison with the organic analogue could not be obtained in the present work as photolysis of *o*-tert-butylnitrobenzene produced a mixture of free radicals as evidenced by an asymmetrical ESR spectrum, despite attempts to eliminate secondary radical production by varying the temperature of the sample (−30 to +25°). In order to clarify the situation we prepared the free radical anion of *o*-(trimethylsilyl)nitrobenzene (see Fig. 1) by allowing *o*-(trimethylsilyl)nitrobenzene to react with potassium in 1,2-dimethoxyethane *in vacuo*. The nitrogen hyperfine splitting was 0.974 millitesla (*cf.* 1.033 mT for nitrobenzene free radical anion under the same conditions[14]). This result is in contrast to that for the free radical anions of *o*-tert-butylnitrobenzene and nitrobenzene (a_N is 1.49[15] and 1.032[12] mT respectively) both obtained under a different set of conditions. The data for the two substituted nitrobenzenes again

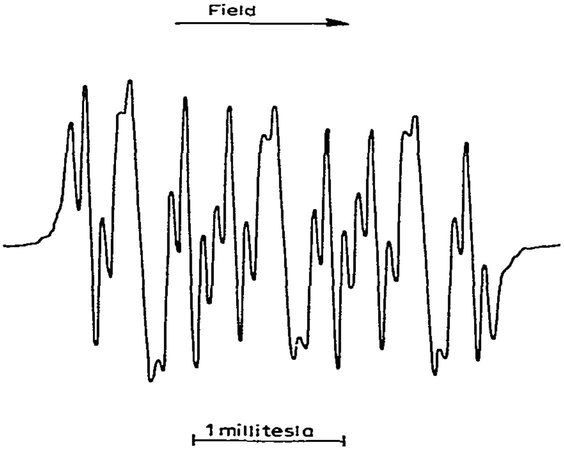


Fig. 1. ESR spectrum of a freshly-reduced solution of *o*-(trimethylsilyl)nitrobenzene in 1,2-dimethoxyethane containing potassium, showing the incompletely resolved spectrum of the *o*-(trimethylsilyl)nitrobenzene radical anion.

suggest that steric interaction in *o*-(trimethylsilyl)nitrobenzene free radical anions is small. An explanation of the different behaviour of *o*-tert-butyl groups and *o*-trimethylsilyl groups is that the larger silicon atom removes the methyl groups further from the environment of the nitro group than does the carbon atom.

It was hoped to obtain a comparison of the steric effects of *o*-tert-butyl and *o*-trimethylsilyl, by monitoring the hydrogen nuclear magnetic resonance of the

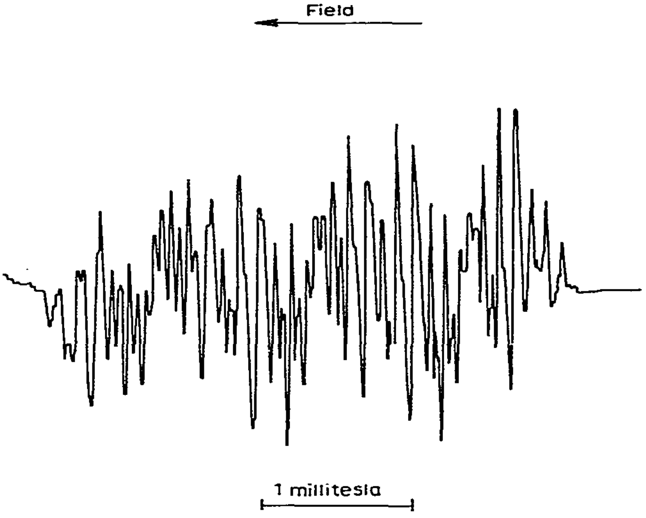


Fig. 2. Conditions as for Fig. 1 but after approximately 30 min had elapsed, showing the presence of decomposition product.

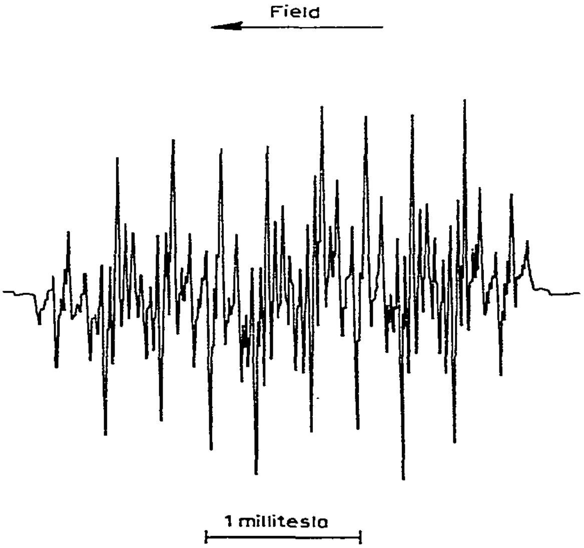


Fig. 3. Conditions as for Fig. 1 but after 1 h had elapsed, showing complete conversion of *o*-(trimethylsilyl)nitrobenzene anion to the nitrobenzene radical anion.

methyl groups of solutions of the *o*-substituted nitrobenzenes in THF, cooled below room temperature: in both cases the methyl hydrogen resonance comprised a single narrow line down to temperatures of −95°.

An interesting observation was made during the attempts to record the ESR spectrum of the *o*-(trimethylsilyl)nitrobenzene anion in solutions sufficiently dilute for good resolution to be possible. During the time taken for dilution the radical seemed to be converted to the nitrobenzene radical anion (Figs. 1, 2 and 3). Also, gas was evolved during the preparation of the former radical anion which suggests that the solutions containing *o*-(trimethylsilyl)nitrobenzene and potassium metal were not completely dry. The hydroxide ion produced may have been responsible for cleavage of the aryl group from the silicon atom: this type of reaction by nucleophiles is known to be facilitated by incorporation of electron-withdrawing groups in the aryl ring[16,17,18].

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