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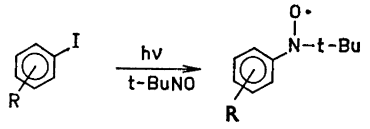
Electron Spin Resonance and Nuclear Magnetic Resonance Spectra of Sterically Hindered Aromatic Nitroxide Radicals. Synthesis of Stable Nitroxide Radicals

JENS A. PEDERSEN and KURT TORSSELL *

Department of Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark

Stable *ortho*-substituted aryl-*t*-butylnitroxides and hydroxylamines have been prepared from *t*-butylmagnesium chloride and the appropriate aromatic nitro compound. The splitting constants were determined in some cases both by ESR and NMR spectroscopy. A good agreement was obtained between the values from the two methods. A simplification of the ESR spectra was attained by the use of deuterated *t*-nitrosobutane as scavenger.

Aromatic nitroxides are conveniently generated by irradiation of iodoarenes in an inert solvent in the presence of *t*-nitrosobutane as a radical scavenger.[1]



In agreement with earlier investigations [2–11] it was found that *ortho*-substituted radicals have relatively high a_N values and the couplings from the aromatic protons could not, or only partially, be resolved. Some of the *ortho*-substituted nitroxides showed, however, a rather well-resolved hyperfine structure, which could only be explained by considering the contribution from the nine protons of the *t*-butyl group. The *t*-butyl group has normally only a slight line-width broadening effect. Furthermore, the free electron distribution in the ring was changed considerably in comparison with the usual *o* : *m* : *p* ratio of *ca.* 2 : 1: 2 in the unhindered derivatives.[2,12] These matters are the object for the present investigation.

ESR SPECTRA

Of the mono-*ortho*-substituted nitroxides only 2-methoxy-, 2-chloro-, 2-bromo-, and 2-trifluoromethylphenyl-*t*-butyl nitroxide gave reasonably

* To whom inquiries should be addressed.

well-resolved ESR spectra. The complexity of the spectra was reduced in the 2,6-di-substituted series. The spectra of 2,4,6-tribromo- and 2,6-dibromo-4-nitrophenyl-*t*-butyl nitroxide were identical, and apart from a line-width broadening effect of the *para*-proton, also identical to the spectrum of 2,6-dibromophenyl-*t*-butyl nitroxide. The same was true for the 2,4,6-trichloro- and 2,6-dichlorophenyl-*t*-butyl nitroxides. This means that the *para*-substituent couples weakly and consequently the spin density in the 4-position is low.

The 3 × 14 line spectrum observed of the di-*ortho*-substituted nitroxides can be explained by assuming that the two *meta*-protons have a coupling constant twice that of the *t*-butyl protons. This was verified by simulation (Figs. 1 and 2). Thus, the special feature of these sterically hindered nitroxides is that the splitting constant for the *t*-butyl protons is increased considerably when this group is rotated out of the plane of ring, and simultaneously the spin distribution is changed significantly in the ring. Calder *et al.*[9] arrived at the same conclusions in a recent study of *ortho*-methyl substituted arylnitroxides.

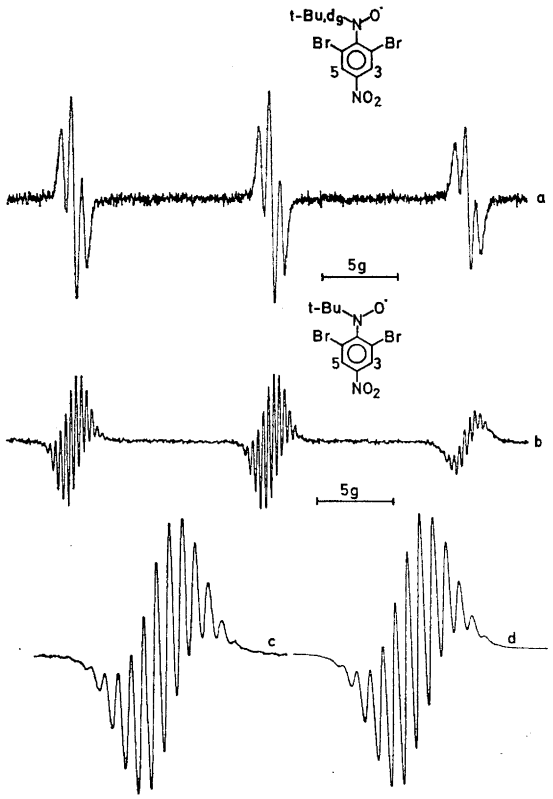


Fig. 1. ESR spectra of 2,6-dibromo-4-nitrophenyl-*t*-butyl nitroxide. a, with the *t*-butyl group deuterated; b, *t*-Bu-H_9; c, M = 0 expanded; and d, M = 0 simulated.

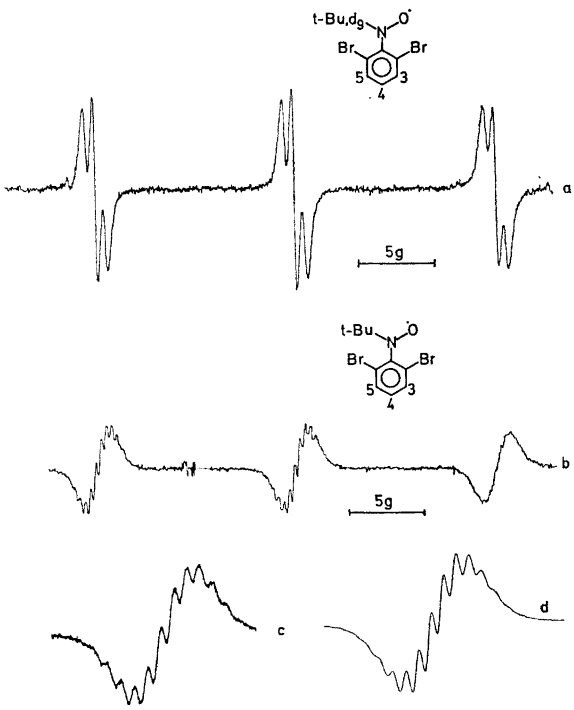


Fig. 2. ESR spectra of 2,6-dibromophenyl-*t*-butyl nitroxide. a, *t*-Bu-d_9; b, *t*-Bu-H_9; c, M = +1 expanded; and d, M = +1 simulated. The *para*-proton causes only a broadening of the line-width.

Because of the line shape of the spectra it may be misleading to rely only on simulation for the determination of splitting constants. This became clear

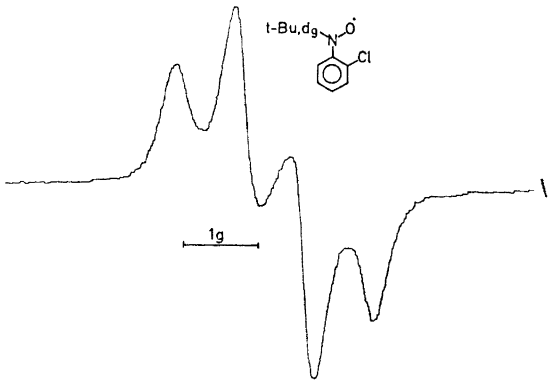


Fig. 3. ESR spectrum of 2-chlorophenyl-*t*-butyl-d_9 nitroxide, M = 0 expanded.

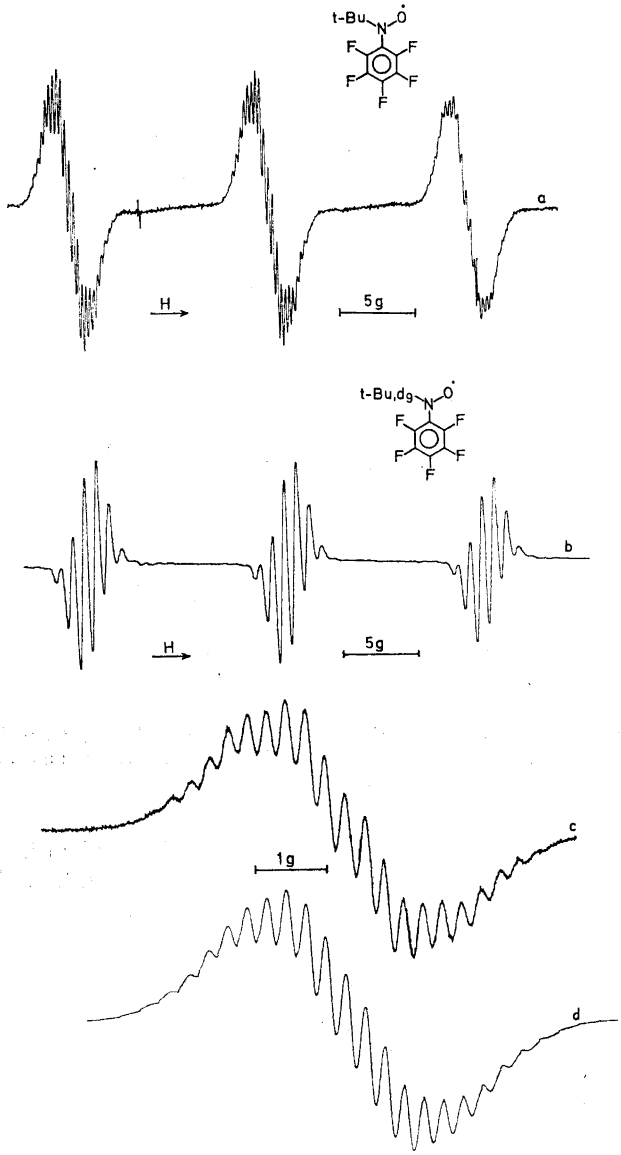


Fig. 4. ESR spectra of pentafluorophenyl-*t*-butyl nitroxide. a, *t*-Bu-H_9; b, *t*-Bu-d_9; c, M = 0 expanded; and d, M = 0 simulated.

from our first analysis of the 2,4,6-tribromophenyl-*t*-butyl nitroxide spectrum where we considered only the contributions by the bromine atoms ($S = 3/2$) and the ring hydrogen atoms. Proper adjustment of line width and intensity gave a rather good fit to the experimental spectrum.

It was therefore decided to eliminate the splitting from the *t*-butyl protons by use of deuterated *t*-nitrosobutane as a scavenger. The splitting of deuterium is 6.55 times smaller than that of the proton, this brings the contribution of *t*-butyl-d_9, group to the hyperfine structure of the spectrum in this series of radicals below the resolution power of the instrument. The effect of the deuteration is demonstrated in an illuminating way in Figs. 1 and 2. The 3×14 line spectrum is reduced to a triplet of triplets, from which the splittings from the *meta*-protons of the 2,6-dibromo-4-nitro- and 2,6-dibromophenyl-*t*-butyl nitroxides can be determined separately. The value agrees excellently with the values obtained from simulation of the original spectra. The method did not work with success for all radicals but in many cases complicated or unresolved spectra were simplified so that all the splittings could be determined. In mono-*ortho*-substituted derivatives the splitting from the *t*-butyl-protons is slightly lower, about 0.25 gauss, than the corresponding coupling in the di-*ortho*-substituted series. The *p*-proton still seems to have a low coupling constant. The *ortho*- and *meta*-protons seem to have about the same coupling constant and this situation is reflected in the spectrum of *o*-chlorophenyl-*t*-butyl-d_9, nitroxide, which shows a triplet of broadened quartets. In Fig. 3 the centre line quartet is depicted. The *p*-proton contributes only to a line-width broadening. Only approximate values for the proton splittings could be obtained by this method, $a_o \sim a_m \sim 0.7$ g. From the NMR spectrum of the radical more exact data were obtained (see below). Fig. 4 shows the spectrum

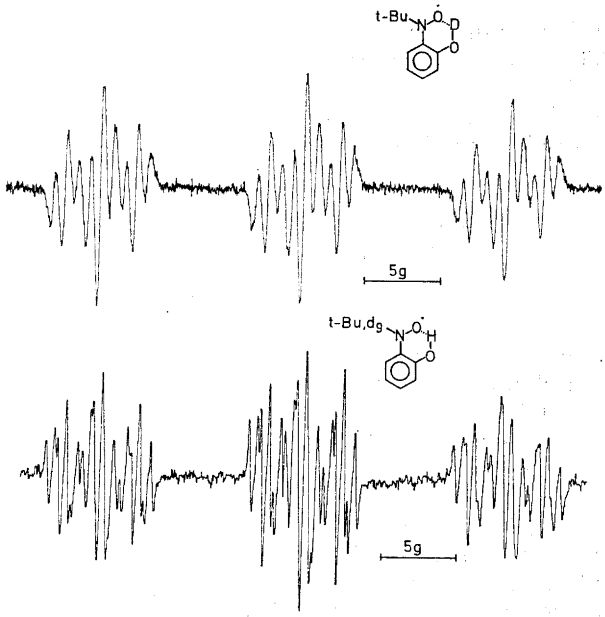
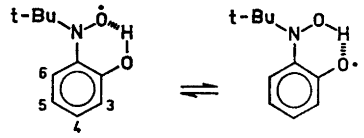


Fig. 5. ESR spectra of 2-hydroxyphenyl-*t*-butyl nitroxide. The smallest splitting is caused by the hydroxy proton, which is proved by deuteration in the upper spectrum. Deuteration of the *t*-butyl group contributes considerably to the sharpening of the lines.

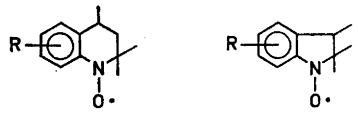
of the pentafluorophenyl-*t*-butyl nitroxide, which proved difficult to analyze by simulation. A considerable simplification was introduced by deuteration, Fig. 4b, which shows that accidentally all fluorine atoms have the same splitting constant, equal to $3 \times a_{t\text{-Bu}}$ (Table 1). From this ratio it was now possible to simulate satisfactorily the experimental spectrum, Fig. 4c and d. The practically identical splittings from all the fluorine atoms contrast sharply to the situation in the sterically hindered perfluoro-triphenylmethyl radical [13] which shows much larger *ortho*- and *para*- than *meta*-splitting. The reason for this is obscure, but might be connected with the more σ-radical-like structure of the nitroxides in comparison to the triphenylmethyls.

The spectrum of o-*hydroxyphenyl*-t-*butyl nitroxide* differed from the spectra of all the other *ortho*-substituted derivatives and resembled closely a spectrum from a sterically unhindered derivative. The *t*-butyl group has a low coupling constant, about 0.1 gauss, and furthermore the $o : m : p$ ratio is close to the normal value, Fig. 5. Apparently, the nitroxide group is forced into the plane of the aromatic ring by hydrogen bonding, but it appears from the coupling constant that the structure resembles more a nitroxide than a phenoxy radical.



Exchange with deuterium proved that the hydroxy proton had the coupling constant of 0.59 gauss. The 0.59 gauss doublets have collapsed to somewhat broadened singlets.

Rozantsev *et al.*[14–16] have studied a series of cyclic nitroxides derived from substituted tetrahydroquinolines or indolines:



In these cases the $o : m : p$ ratio is $\sim 3 : 1 : 3$ indicating that the nitroxide function is in the plane of the aromatic ring.

If it is assumed that the higher a_N values of the mono-*ortho*-substituted nitroxides (*ca.* 1 – 2 gauss larger) are a result of steric hindrance and broken conjugation between the ring and the substituent, one anticipates that the di-*ortho*-substituted nitroxides should show still higher a_N values. However, this is not the case; the di-*ortho*-substituted radicals have *ca.* 1 gauss lower a_N values than the mono-*ortho*-substituted nitroxides. The explanation that two electron-withdrawing groups, such as Cl, Br, OCH_3 ($-I$), in the *ortho* position would decrease the spin density on nitrogen purely by inductive effects, is not entirely satisfactory, since two *o*-methyls ($+I$) also cause a slight decrease of the N-splitting (Table 1). The *ortho*-substituents have apparently an effect on the spin distribution within the N – O group.

Table 1. Splitting constants of nitroxide radicals, Ar—NO·—*t*-Bu, prepared in the cavity by UV irradiation of the corresponding iodides in methylene chloride at −50° in the presence of *t*-nitrosobutane.

Substituted phenyl-*t*-butyl nitroxide	Hfs. constant, gauss	
	a_N[c]	Other nuclei, remarks
2,5-Dibromo-4-iodo-	13.8	[a]
2,5-Dibromo-	14.1	[a]
2,4,5-Tribromo-	13.9	[a]
2-Chloro-4-bromo-	13.8	[a]
2,4-Dinitro-	11.4	[a]
2-Methyl-	14.0	[a,b]
2-Iodonaphthalene	12.2	[a]
2,4,6-Trinitro-	12.0	partly resolved hfs. *ca.* 0.25 gauss
2,6-Dibromo-4-nitro-	13.0	$a_3=a_5=0.66$, $a_{t\text{-Bu}}=0.33$
2,4,6-Tribromo-	13.1	$a_3=a_5=0.65$, $a_{t\text{-Bu}}=0.33$
2,6-Dibromo-	13.2	$a_3=a_5=0.64$, $a_4\sim 0.1$, $a_{t\text{-Bu}}=0.32$
2,4,6-Trichloro-	13.0	$a_3=a_5=0.68$, $a_{t\text{-Bu}}=0.34$[f]
2,6-Dichloro-	13.1	$a_3=a_5=0.69$, $a_4\sim 0.1$, $a_{t\text{-Bu}}=0.35$
2,6-Dimethoxy-	13.3	$a_3=a_5=0.69$, $a_4\sim 0.1$, $a_{t\text{-Bu}}=0.33$[g]
2,6-Dimethyl-	13.8	$a_3=a_5=0.78$[h]
2-Chloro-	14.0	$a_3=+0.49$, $a_4=-0.28$, $a_5=+0.82$, $a_6=-0.78$, $a_{t\text{-Bu}}=-0.24$[i,j]
2-Bromo-	14.2	$a_3=+0.44$, $a_4=-0.26$, $a_5=+0.82$, $a_6=-0.76$, $a_{t\text{-Bu}}=-0.25$[i,k]
2-Methoxy-	14.5	$a_3=+0.61$, $a_4=-0.41$, $a_5=+0.87$, $a_6=-0.99$, $a_{OCH_3}=+0.063$, $a_{t\text{-Bu}}=-0.26$[i,l]
2,3,4,5,6-Pentafluoro-	13.1	$a_F=0.79$, $a_{t\text{-Bu}}=0.26$
2-Trifluoromethyl-	13.6	not determined
2-Fluoro-	14.2	$a_3=+0.58$, $a_4=-0.56$, $a_5=+0.90$, $a_6=-1.04$, $a_F=+1.35$, $a_{t\text{-Bu}}=-0.25$[i,m]
2-Hydroxy-	13.5	$a_3=a_5=0.76$, $a_4=a_6=2.45$, $a_{OH}=0.59$
3,5-Dibromo-	11.8	$a_2=a_4=a_6=2.18$
4-Iodo- [d]	12.2	$a_2=a_6=2.17$, $a_3=a_5=0.95$
3-Iodo-	12.4	$a_2=a_4=a_6=2.04$, $a_5=0.78$
3-Chloro- [e]	12.1	$a_2=a_4=a_6=2.10$, $a_5=0.85$
4-Methoxy-	13.2	$a_2=a_6=1.9$, $a_3=a_5=0.8$
3-Methoxy- [e]	12.5	$a_2=a_4=a_6=1.94$, $a_5=0.78$[m]
3-Methyl- [e]	12.8	$a_2=a_4=a_6=1.9$, $a_5=a_{CH_3}=0.65$
4-Chloro- [d]	12.4	$a_2=a_6=2.1$, $a_3=a_5=1.0$
4-Bromo- [d]	12.3	$a_2=a_6=2.14$, $a_3=a_5=0.95$
4-Methyl- [d]	13.0	$a_2=a_6=a_{CH_3}=2.00$, $a_3=a_5=0.92$
3-Carboxy-	12.6	$a_2=a_4=a_6=1.95$, $a_5=0.90$

[a] Could not be resolved even by use of *t*-BuNO-d_9. [b] *Cf.* Ref. 9. [c] ± 0.05 gauss. [d] *Cf.* Ref. 12.
[e] *Cf.* Barbarella, G. and Rassat, A. *Bull. Soc. Chim. France* **1969** 2378.
[f] The NMR measurements gave $a_3=a_5=+0.66$ gauss and *t*-Bu = −0.34 gauss (300°K).
[g] *Cf.* Ref. 11. NMR gave $a_3=a_5=+0.70$ gauss, $a_4=-0.17$ gauss, and $a_{t\text{-Bu}}=-0.31$ gauss (295°K).
[h] *Cf.* Ref. 9. NMR gave $a_3=a_5=+0.70$ gauss (295°K).
[i] Calculated from the NMR spectrum (300°K).
[j] According to the ESR spectrum the deuterated radical showed a broadened quartet with an average splitting of *ca.* 0.7 gauss (3H) and it was concluded that the *p*-proton probably had a coupling close to the line-width at half peak height, *ca.* 0.3 gauss. Fig. 3.
[k] *Cf. j*, broadened quartet, *ca.* 0.8 gauss (3H) and one proton *ca.* 0.3 gauss.
[l] The ESR spectrum of the deuterated radical had rather complicated features.
[m] *Cf.* Jakobsen, H. J., Petersen, T. E. and Torssell, K. *Tetrahedron Letters* **1971** 2913.

NMR SPECTRA

It was desirable to obtain more reliable data and to confirm our assignments for the more complicated radicals, *e.g.*, mono-*ortho*-substituted radicals. Suitable nitroxides were therefore synthesized and their NMR spectra recorded. The direction and magnitude of the shift with reference to the parent diamagnetic compound determine the signs and magnitudes of the splittings. Equation (1) [17] relates the splitting constant (in gauss) for a nucleus i, $S=\frac{1}{2}$, 300°K with the shift ΔH_i in ppm (positive in the upfield direction)

$$a_i = -1.35 \times \Delta H_i \times 10^{-2} \text{ gauss} \quad (1)$$

The observation of the NMR peaks, which are greatly broadened, is facilitated by a high concentration of the radical in the solvent; this decreases the electron exchange relaxation time.[18] In one case a radical solvent, t-$Bu_2NO\cdot$, was used for the recording of NMR spectra of phenoxy radicals.[19]

The present method was recently used for some other nitroxides,[9,11] and we give here further examples of the determination of splitting constants by independent methods. There are very few instances, where it is possible to observe both the NMR and ESR spectra of the same radical and to compare the splitting constants by the two methods. As expected, the shifts as well as the line width of the absorption peaks are very large. Fig. 6 shows the spectrum of *o*-bromophenyl-*t*-butylnitroxide. The *ortho*-, *para*-, and *t*-butyl-protons are shifted to higher field, whereas the *meta*-protons are shifted down-

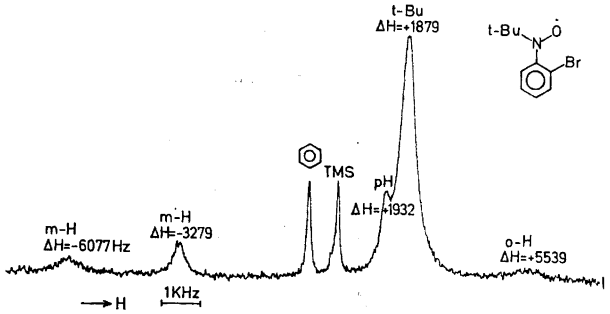


Fig. 6. The NMR-spectrum of 2-bromophenyl-*t*-butyl nitroxide.

field. The compounds giving well-resolved ESR and NMR spectra showed good agreement between the coupling parameters determined, although widely different experimental conditions were used in the two methods. The center quartet of the *o*-chlorophenyl nitroxide spectrum, Fig. 3, which seemed to arise from three equivalent protons could be synthesized with help of the somewhat different constants obtained from the NMR spectrum (Table 1) by proper adjustment of the line-width.

SYNTHESIS

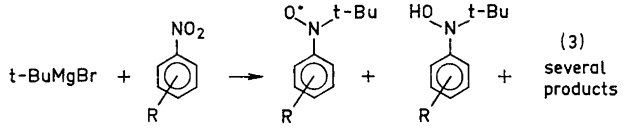
t-Nitrosobutane-d_9, was synthesized in an overall yield of 26 % from *t*-butylamine-d_9, according to (2)

$$t\text{-BuNH}_2\text{-}d_9 \xrightarrow{KMnO_4} t\text{-BuNO}_2\text{-}d_9 \xrightarrow[\text{red. HCl}]{\text{electrolytic}}$$

$$t\text{-BuNHOH-}d_9\cdot\text{HCl} \xrightarrow[Br_2]{OH^-} t\text{-BuNO-}d_9 \qquad (2)$$

This route seems to be best also for large scale preparations. *

Most nitroxides are rather short-lived, but among the aryl-*t*-butylnitroxides those with *ortho*-substituents or blocking groups in the *para*-position can be prepared in a pure form.[8,20] Since sterically hindered *ortho*-substituted nitroxides were of primary interest to us, a series of aryl-*t*-butylnitroxides were synthesized. Several methods for the preparation of nitroxides have been described.[21,22] Reaction (3) seemed to present the simplest preparative route,[23] although the yields are low. Large amounts of by-products are formed, but the nitroxides could be separated together with the corresponding hydroxylamine and amine by high vacuum distillation. Fractional crystallization and preparative thin layer chromatography on silica was used for the final purification. The hydroxylamines could be oxidized quantitatively to the nitroxides by silver oxide.[23]



The *ortho*-substituted nitroxides are red, low-melting and rather stable solids. The physical and analytical data are collected in Table 2.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded at 100 MHz on a Varian HA-100 spectrometer operating at the HR-mode with a modulation frequency of 15 KHz. Chloroform was used as solvent. The ESR spectra were run on a Varian E3 instrument. A flat cell was used inserted in a variable temperature accessory.

Generation of aryl-t-butylnitroxides. The iodides, *ca.* 100 mg, were dissolved in deaerated methylene chloride (0.5 ml) and a few crystals of *t*-nitrosobutane were added. Irradiation of the sample at −50°C by light from a high pressure Hg lamp, 500 W, filtered by 1 M $CuSO_4$ solution, produced within few minutes the nitroxides in an amount sufficient for the recording of their spectra.

Synthesis of t-*nitrosobutane*-d_9. *t*-Butylamine-d_9, (Merck, Sharp and Dohme, Canada; 3 g) was oxidized by potassium permanganate to *t*-nitrobutane,[24] and the crude product was reduced electrolytically to the hydroxylamine hydrochloride,[25] which was then without any purification oxidized to the nitroso compound by bromine.[26] Four equivalents of sodium hydroxide in proportion to the *t*-butyl hydroxylamine hydrochloride were used. The deuterated nitroso compound precipitated from the aqueous solution and was

* Added in proof. *t*-BuNO-d_9 was recently prepared by another method, *cf. J. Chem. Soc.* **C 1971** 2324.

Table 2. Physical and analytical data for aryl-*t*-butyl hydroxylamines and aryl-*t*-butylnitroxide radicals.

Aryl	Hydroxylamine							Nitroxide		
	Mol. weight	m.p. °C	UV absorption λ mμ	ε	Calc. C %	H %	Found C %	H %	m.p. °C	UV absorption λ mμ	ε
2-Chlorophenyl	199.6	117	255 212	2200 8760	60.14	7.07	60.19	7.02	43–44	290 250 sh 212	1600 2250 11000
2-Bromophenyl	244.1	118	281 240 211	2760 2930 12700	49.16	5.78	49.32	5.79	51–53	294 244 sh 211	1370 3350 12000
2-Methoxyphenyl	195.3	186	280 240 212	2450 2800 10600	67.69	8.78	67.66	8.71	47–49	289 sh 281 219	2040 3060 6830
2,4,6-Trichlorophenyl	268.5	118	—	—	44.88[a]	4.14	45.54	4.33	61–62	313 220	905 9200

[a] Analysis of the nitroxide.

filtered off and dried. Extraction with methylene chloride gave an additional small amount of the nitroso compound. It was used directly as a scavenger without any further purification. 900 mg (26 %) of crude product was obtained.

t-*Nitrosobutane*-H_9, was prepared according to the same method. It was recrystallized from a mixture of cyclohexane and petrol ether.

Aromatic iodides. Most of the iodides were commercially available, others were prepared by conventional methods. *2,6-Dimethoxy-iodobenzene* was prepared from 2,6-dimethoxyphenyl lithium [27] by addition of one molar equivalent of iodine. The reaction mixture was hydrolyzed with acidified water and the iodo compound was isolated from the organic phase by evaporation of the solvent and crystallization of the residue from cyclohexane, m.p. 107 – 109°. The yield was 60 %.

ortho-*Substituted aryl*-t-*butylnitroxides*. o-*Bromophenyl*-t-*butylnitroxide and* o-*bromophenyl*-t-*butylhydroxylamine*. To the Grignard reagent, *ca.* 2.5 equiv., prepared from magnesium (10.2 g) and *t*-butyl chloride (38 g) in ether (150 ml), 2-bromo-nitrobenzene (25 g) dissolved in ether (50 ml) was added slowly at −70°. The temperature was raised to 25°C and left there for a couple of hours. The mixture was hydrolyzed with ice and saturated ammonium chloride solution. The organic phase was separated, dried with sodium sulphate, and evaporated. The darkbrown residue was distilled *in vacuo* (slight decomposition) and the reddish-brown fraction boiling at 85 – 95° (10^{-2} – 10^{-3} mm) was collected (11.5 g). It consisted mainly of a mixture of *2-bromophenyl*-t-*butyl nitroxide*, *2-bromophenyl*-t-*butyl hydroxylamine*, and *2-bromophenyl*-t-*butylamine*. By adding petrol ether part of the *hydroxylamine*, 2.1 g, crystallized from the mixture on standing in the refrigerator, m.p. 114 – 116°. The rest, separated by preparative TLC, afforded 0.9 g of the hydroxylamine and 1.1 g of the nitroxide. The *nitroxide* melted at 53°, dark red crystals.

The *2-fluoro-*, *2-chloro-*, *2-methoxy-*, *and 2,4,6-trichlorophenyl* derivatives were prepared according to the same method. Analytical and physical data are collected in Table 2.

Occasionally, part of the hydroxylamine could be separated by addition of petrol ether to the crude product and cooling the mixture in a freezer.

Oxidation of 2-bromophenyl-t-butyl hydroxylamine with silver oxide. The hydroxylamine (1.0 g) dissolved in benzene (7 ml) was stirred with silver oxide (0.8 g) for 3 h at room temperature. The solution became rapidly dark-red. It was filtered and evaporated. The viscous oil, which solidified on standing in the refrigerator, consisted of practically pure *nitroxide*, m.p. 53°C. Its NMR spectrum showed a trace of the hydroxylamine. The radical is stable when stored in the freezer.

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