

nitroxide. After removal of a small amount of sodium chloride, the ether was removed by evaporation *in vacuo*, and the residue 7.63 g., 58%, consisted of crude N,N-di-*t*-butylhydroxylammonium chloride. After one recrystallization from acetonitrile, it was isolated pure, m.p. 184° dec., 5.2 g., 39%. In other experiments, the solid was isolated and suspended in glyme prior to its hydrolysis with aqueous sodium borohydride. The results were similar. In control experiments it was established that di-*t*-butylnitroxide was inert to either aqueous or glyme solutions of sodium borohydride over extended periods of time at room temperature.

**Reaction of Phenylsodium with *t*-Nitrobutane.**—*t*-Nitrobutane (52.5 g., 0.5 mole) was added slowly to a vigorously stirred slurry of phenylsodium prepared from 23 g. (1.0 g.-atom) of sodium and 56.3 g. (0.5 mole) of chlorobenzene in 150 ml. of toluene.<sup>28</sup> The temperature of the reaction mixture during the addition was maintained at or slightly below 0°. After standing overnight at room temperature a portion of the reddish colored slurry was removed and centrifuged. The solid was washed several times with cyclohexane and dried at room temperature *in vacuo*. In order to prevent exposure to atmospheric moisture these operations were carried out in a nitrogen-filled drybox. The colorless solid so obtained was found to be diamagnetic by e.s.r., containing of the order of 10<sup>16</sup> free spins/g. Its infrared spectrum (Nujol mull) is shown in Fig. 1C. When added to water it reacted instantly to give a mixture of *t*-butylphenylnitroxide,<sup>8</sup> N-*t*-butylaniline, and N-*t*-butyl-N-phenylhydroxylamine. In similarity to I, this solid reacted in the dark with a 2 × 10<sup>-3</sup> M aqueous solution of luminol with distinct blue chemiluminescence. Chemiluminescence was absent during hydrolysis in the absence of luminol.

**Reaction of *t*-Nitrobutane with Sodium in the Presence of Tritiated *t*-Nitrosobutane.**—*t*-Nitrosobutane<sup>29</sup> was tritiated by the gas exposure method of Wilzbach.<sup>30</sup> After removal of tritium by pumping the sample at -180° and 0.001 mm. for 2 to 3 hr., the total activity was 30.7 × 10<sup>8</sup> d.p.m. This material (0.6793 g., 6.8 mmoles) was added at the outset of reaction to a run of 10.3 g. (100 mmoles) of *t*-nitrobutane and 2.3 g. (0.1 g.-atom) of sodium in 150 ml. of glyme. The reaction, run as usual, was filtered after disappearance of all the metal. The solid product was washed with several 50-ml. portions of ether and rapidly dried *in vacuo* to give 10 g. of isolated material. A representative sample of this material showed that the total activity in the solid was 11.4 × 10<sup>6</sup> d.p.m. After pumping on the solid for 3 hr. at

room temperature at 0.1 mm., it lost all its activity but retained its ability to form di-*t*-butylnitroxide. Hydrolysis of 6.1723 g. of solid, covered with 50 ml. of heptane, with 15 ml. of water at 0-4° gave the results shown in Table VII.

TABLE VII

PRODUCTS OF HYDROLYSIS OF SOLID OBTAINED FROM THE REACTION OF *t*-C<sub>4</sub>H<sub>9</sub>NO<sub>2</sub> WITH SODIUM IN THE PRESENCE OF TRITIATED *t*-C<sub>4</sub>H<sub>9</sub>NO

Product	(t-C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> -N-O				
	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub> NO	<i>t</i> -C <sub>4</sub> H <sub>9</sub> OH	<i>t</i> -C <sub>4</sub> H <sub>9</sub> NO <sub>2</sub>	N-O
mmoles per 10 g. of solid	1.5	10.0	3.1	1.2	9.9
Wt. %	0.8	8.7	2.3	1.3	14.3

The filtrate had a total activity of 5.40 × 10<sup>8</sup> d.p.m. (17.5% of the starting total) and contained 1.52 g. of tri-*t*-butylhydroxylamine. Isolation of a portion of this product by preparative v.p.c. established that it was responsible for 2.41 × 10<sup>6</sup> d.p.m. or roughly 45% of the total activity remaining in the filtrate. The low recovery of activity is undoubtedly due to loss of volatile products (presumably isobutylene).

**Reduction of Di-*t*-butylnitroxide by Sodium.**—Sodium metal (1.12 g., 0.048 g.-atom) was added under a nitrogen blanket to 100 ml. of anhydrous glyme containing 7.2 g. (0.05 mole) of di-*t*-butylnitroxide. The reaction mixture was stirred at room temperature for 2 days. At the end of this time most of the sodium had reacted and a clear colorless solution resulted. Addition of hydrogen chloride to the filtered solution resulted in the formation of N,N-di-*t*-butylhydroxylammonium chloride; 7.2 g., 80%.

**Reaction of Sodium Peroxide with *t*-Nitrosobutane.**—To a solution of 11.6 g. (0.04 mole) of ferrous sulfate in 40 ml. of water was added a solution of 1.7 g. (0.02 mole) of *t*-nitrosobutane dimer in 50 ml. of freshly distilled glyme. Sodium peroxide (1.6 g., 0.02 mole), was added gradually with shaking. After standing for 1 hr. at room temperature with occasional shaking, a sample of the green glyme layer was found to be approximately 10<sup>-3</sup> M in di-*t*-butylnitroxide by e.s.r. No tri-*t*-butylhydroxylamine could be detected by v.p.c.

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(28) J. F. Nobis and L. F. Moormeier, *Ind. Eng. Chem.*, **46**, 539 (1954).(29) W. D. Emmons, *J. Am. Chem. Soc.*, **79**, 6522 (1957).(30) K. E. Wilzbach, *ibid.*, **79**, 1013 (1957).

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## Reactions of Organoalkali Compounds with Nitro Compounds: A New Synthesis of Nitroxides

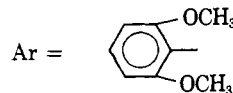
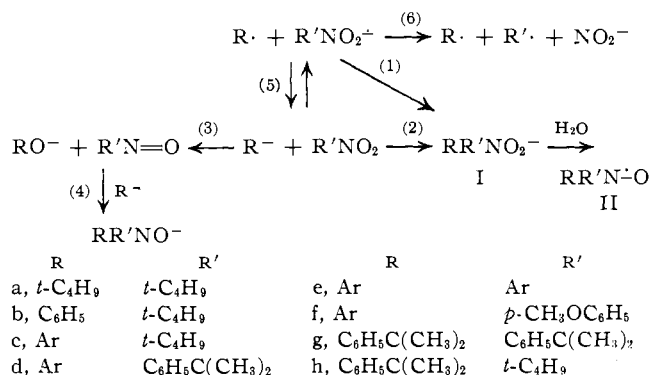
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The reaction of carbanions with nitro compounds may take one of several routes. Attack may occur directly at the nitrogen atom of the nitro group to give an intermediate (presumed to be a hydroxylamine oxide salt) which on hydrolysis affords nitroxide. Carbanion may also reduce the nitro compound to its anion radical or it may attack at the oxygen atoms of the nitro group.

### Introduction

It has been shown in the previous publication<sup>1</sup> that di-*t*-butylnitroxide (IIa) results from hydrolysis of a diamagnetic salt formed during the reduction of *t*-nitrobutane with metallic sodium. Evidence was presented that the structure of this salt is sodium N,N-di-*t*-butylhydroxylamine oxide (Ia) arising by the combination of a *t*-butyl radical with the *t*-nitrobutyl anion radical (1).<sup>1,2</sup> An analogous compound Ib, prepared by the reaction of phenylsodium with *t*-nitrobutane (2), on hydrolysis gives *t*-butylphenylnitroxide (IIb). This suggested that a convenient route to nitroxides lay at hand in the reactions of anions with nitro compounds, which is the subject of this paper.

(1) A. K. Hoffmann, A. M. Feldman, E. Gelblum, and W. G. Hodgson, *J. Am. Chem. Soc.*, **86**, 639 (1964).(2) A. K. Hoffmann, W. G. Hodgson, D. L. Maricle, and W. H. Jura, *ibid.*, **86**, 631 (1964).

## Results

*t*-Butylphenylnitroxide (IIb), was prepared by hydrolysis of Ib in a 30% yield as determined by e.s.r. Although too unstable to withstand extensive purification, it could be obtained from the crude hydrolysate in a purity of about 50% as determined by magnetic susceptibility. The major impurities which could not be completely separated were *N*-*t*-butylaniline and *N*-*t*-butyl-*N*-phenylhydroxylamine. Oxidation of the latter by silver oxide in pentane gave *t*-butylphenylnitroxide in an increased purity of roughly 80%. The e.s.r. spectrum of this nitroxide is fully consistent with one in which the odd electron interacts with a nitrogen atom and a phenyl ring. A similar reaction between *t*-nitrobutane and phenyllithium gave a lower yield, 15%, of crude *t*-butylphenylnitroxide.

*t*-Nitrobutane also reacted with *t*-butyllithium to give di-*t*-butylnitroxide after hydrolysis. Although less convenient for the preparation of di-*t*-butylnitroxide than direct reaction between sodium and *t*-nitrobutane,<sup>1</sup> the reaction of anions with nitro compounds is useful for other, in particular unsymmetrical, nitroxides. 2,6-Dimethoxyphenyllithium was chosen for this study because of the known stabilization of nitroxides by methoxy groups<sup>3a-c</sup> and the ready availability<sup>4</sup> of this reagent. It reacted with *t*-nitrobutane, 2-phenyl-2-nitropropane (*t*-nitrocumene), 2,6-dimethoxynitrobenzene, and *p*-nitroanisole to give, after hydrolysis, the corresponding nitroxides IIc-IIf, respectively. These nitroxides were isolated as crystalline solids containing one free spin per molecule and exhibited no tendency to decompose or dimerize at room temperature in the dark. The yields reported in Table I are probably not maximal because no efforts were made to improve them. In contrast to 2,6-dimethoxyphenyllithium, the reaction of cumyl potassium with *t*-nitrocumene gave only trace amounts of di-*t*-cumylnitroxide with bicumyl as the major product. *t*-Nitrobutane also reacted with cumyl potassium to give bicumyl in a complex mixture containing twenty-two components. *t*-Nitrosobutane, di-*t*-butylnitroxide, and tri-*t*-butylhydroxylamine were also recognized in this mixture but the remaining products have not been identified.

TABLE I  
PROPERTIES OF NITROXIDE RR'NO· (II)

Compound	Yield, <sup>a</sup> %	M.p., °C.	g- value	h.c.c., gauss	Effective magnetic moment, B.M.
IIa	38, <sup>b</sup> (15) <sup>c</sup>	.....	2.0065	$a_N = 15.25$	1.72
IIb	(30), <sup>d</sup> (15) <sup>e</sup>	.....	.....	$a_N = 12.50$ $a_o = a_p = 2a_m = 1.82$	..
IIc	17.8	101-102.5	2.0062	$a_N = 13.22$	1.73
IId	11.8	77-78	2.0060	$a_N = 13.19$	1.74
IIe	4.2	199-200	2.0067	$a_N = 10.17$	1.74
IIf	1.0 (15)	114.5-115	2.0055	$a_N = 10.10$ $a_o = 2.61$	..

<sup>a</sup> Values in parentheses were determined by e.s.r.; the others were determined by isolation. <sup>b</sup> From sodium and *t*-nitrobutane. <sup>c</sup> From *t*-butyllithium and *t*-nitrobutane. <sup>d</sup> From phenylsodium and *t*-nitrobutane. <sup>e</sup> From phenyllithium and *t*-nitrobutane.

Attempts to utilize Grignard reagents in these reactions met largely with failure in a preparative sense. *t*-Butylmagnesium chloride reacted with *t*-nitrobutane to give only small amounts of di-*t*-butylnitroxide and acted predominantly as a reducing agent, producing *t*-nitrosobutane as the major nitrogen containing product. No nitroxide could be isolated from the

(3) (a) K. H. Meyer and H. G. Billroth, *Ber.*, **52**, 1476 (1919); (b) K. H. Meyer and W. Reppe, *ibid.*, **54**, 327 (1921); (c) M. B. Neiman and A. L. Buchachenko, *Izvest. Akad. Nauk. S.S.S.R.*, **10**, 1742 (1961).

(4) G. Wittig, "Organic Reaction. s." Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 288.

interaction of *p*-anisylmagnesium bromide and *p*-nitroanisole.

## Discussion

The reaction of an anion with a nitro compound may take three courses: (a) attack at the nitrogen atom of the nitro group (2) resulting in I, (b) attack at the oxygen atoms of the nitro group (3) suggested by the formation of phenoxide salts and N,N-disubstituted hydroxylamines (4), and (c) electron exchange between anion and nitro compound (5) resulting in nitro anion radical and radical. Facile reduction of nitro compounds to their anion radicals by anions finds recent precedent in the reductions of aromatic nitro compounds by *t*-butoxide ion,<sup>5</sup> and in the electron exchange between dinitrodurene dianion and dinitrodurene.<sup>6</sup> Such electron exchanges are not limited to nitro compounds. Thus, the conversion of alkyl halides to free radicals<sup>7,8a,b</sup> by lithium alkyls presumably involves intermediate unstable halide anion radicals as postulated for electroreductive processes.<sup>9</sup> More stable anion radicals may be generated by the reduction of aromatic hydrocarbons by anions<sup>10</sup> while electron exchange between anion radicals or dianions with their corresponding neutral molecules is well known.<sup>11</sup> The available evidence suggests that such electron transfers are rapid, bordering on diffusion control.<sup>12a,b,13</sup> For example,  $k_{exch}$  for naphthalenide ion and naphthalene in 1,2-dimethoxyethane ranges from  $10^7$  to  $10^9$  l. mole<sup>-1</sup> sec.<sup>-1</sup> for the potassium and sodium salts, respectively.

In these reactions the formation of significant amounts of nitroxide after hydrolysis is taken to signify the presence of I. Since cumyl anion and *t*-nitrocumene afford bicumyl as the major product with only traces of di-*t*-cumylnitroxide, it is apparent that cumyl radicals are formed to the virtual exclusion of Ig. This result indicates the operation of (5) and is in accord with the observed oxidation-reduction potentials of this reactant pair.<sup>2</sup> The cumyl radicals arising from electron exchange, augmented by those from the collapse of the *t*-nitrocumyl anion radical (6), cannot be scavenged by this short-lived intermediate and therefore dimerize. As evidenced by the formation of di-*t*-butylnitroxide and tri-*t*-butylhydroxylamine, *t*-nitrobutane is also reduced to its anion radical by cumyl anion<sup>1</sup> in agreement with observed oxidation-reduction potentials.<sup>2</sup> For this reactant pair it was hoped that combination of cumyl radicals with relatively long-lived *t*-nitrobutyl anion radicals would give Ih. The corresponding nitroxide was not isolated but may, nevertheless, be present in the reaction mixture.<sup>14</sup>

Like the cumyl anion, *t*-butyl anion is capable of reducing *t*-nitrobutane. In view of the ease with which such electron transfers occur, Ia is considered to arise *via* 5 and 1 rather than by 2. The sequence 5 followed by 1, however, is not intended to imply that electron exchange is concerted with or immediately

(5) G. A. Russel and E. G. Janzen, *J. Am. Chem. Soc.*, **84**, 4153 (1962).

(6) D. H. Geske, J. L. Ragle, M. Bambenck, and A. L. Balch, Abstracts of Papers, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1962, p. 10T.

(7) D. Bryce-Smith, *J. Chem. Soc.*, 1603 (1956).

(8) (a) F. S. Dyachkovskii and A. E. Shilov, *Zh. Obshch. Khim.*, **33**, 406 (1963); (b) F. S. Dyachkovskii, N. N. Bubnov, and A. E. Shilov, *Doklady Akad. Nauk S.S.S.R.*, **123**, 870 (1958).

(9) N. S. Hush, *Z. Elektrochem.*, **61**, 734 (1957).

(10) H. W. Brown and R. C. Jones, *J. Chem. Phys.*, **36**, 2809 (1962).

(11) For a summary of numerous examples see G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Am. Chem. Soc.*, **84**, 4155 (1962).

(12) (a) R. L. Ward and S. I. Weissman, *ibid.*, **80**, 1398 (1958); (b) M. T. Jones and S. I. Weissman, *ibid.*, **84**, 4269 (1962).

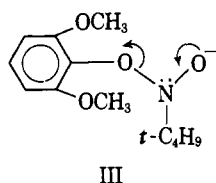
(13) H. Diebler, M. Eigen, and P. Matthies, *Z. Naturforsch.*, **16b**, 629 (1961).

(14) It would not be possible to detect *t*-butyl-*t*-cumylnitroxide in the presence of di-*t*-butylnitroxide by e.s.r. since their h.c.c.'s are expected to be too close for resolution.

followed by bond formation since such a process is chemically indistinguishable from 2. In order for the two routes to be distinguishable, the radical and nitro anion radical must diffuse apart prior to combination. Indeed, evidence for the presence of *t*-butyl radicals in solution is provided by the formation of tri-*t*-butylhydroxylamine.<sup>1,15</sup>

In contrast to cumylpotassium, 2,6-dimethoxyphenyllithium reacted with *t*-nitrobenzene to give, after hydrolysis, significant amounts of II<sub>d</sub> and essentially no bicumyl, indicating direct attack of the anion on the nitro group. Since 2,6-dimethoxyphenyl anion is undoubtedly more difficult to oxidize to the corresponding radical than cumyl anion, this behavior is not unexpected. The reaction of 2,6-dimethoxyphenyllithium with *t*-nitrobenzene probably also proceeds *via* 2 since *t*-nitrobenzene is reduced at approximately the same potential as *t*-nitrobenzene.<sup>2</sup> The detection of only traces of di-*t*-butylnitroxide or sodium nitrite from the reaction of phenylsodium with *t*-nitrobenzene suggests that this reaction occurs similarly. Since aromatic nitro compounds generally have reduction potentials roughly 0.5 v. lower than aliphatic nitro compounds,<sup>16</sup> it remains unknown whether (5, 1) is operational during the formation of Ie and If. Further insight into this question awaits determination of the oxidation-reduction potentials of the various reactants.

In addition to attack at the nitrogen atom, anions also appear to attack at the oxygen atoms of the nitro group. The formation of N-*t*-butyl-N-(2,6-dimethoxyphenyl)-hydroxylamine from the reaction of 2,6-dimethoxyphenyllithium with *t*-nitrobenzene is considered to arise *via* 3 and 4. Compound III is similar to the intermediate proposed earlier<sup>1</sup> as a precursor of



*t*-nitrosobutane during the reduction of *t*-nitrobenzene by sodium and is consistent with the formation of lithium 2,6-dimethoxyphenoxide. Ample precedent for 4 exists since the reaction of Grignard reagents with nitroso compounds is well known to result in N,N-disubstituted hydroxylamines.<sup>17</sup> N-*t*-Butyl-N-phenylhydroxylamine resulting from the interaction of phenylsodium and *t*-nitrobenzene is presumed to arise by the same route.

### Experimental<sup>18</sup>

Electron spin resonance measurements were made on a Varian V-4500 electron spin resonance spectrometer with a modulation frequency of 100 kc.p.s. Hyperfine coupling constants (h.c.c.) were measured by comparison with the known h.c.c. of peroxyamine disulfonate and should be accurate to  $\pm 0.05$  gauss. The *g*-values were measured by direct comparison with solid 1,1-diphenyl-2-picrylhydrazyl. Susceptibilities were determined on a Gouy balance of standard design using ferrous ammonium sulfate for calibration.

***t*-Butylphenylnitroxide (II<sub>b</sub>).**—*t*-Nitrobenzene (52.5 g., 0.5 mole) was allowed to react with phenylsodium (0.5 mole) by the procedure reported earlier.<sup>1</sup> After standing at room temperature overnight, the reaction mixture was hydrolyzed by the addition of 500 ml. of water. The organic layer was separated,

(15) For reactions involving *t*-nitrobenzene or other nitro compounds yielding anion radicals too unstable to enter 1, the absence of significant amounts of nitroxides results in an "all or nothing" distinction between 2 and 5 followed by 1. In reactions involving *t*-nitrobenzene, whose anion radical is an efficient radical scavenger, the viability of both routes renders an "all or nothing" distinction impossible in the present work.

(16) A. H. Maki and D. H. Geske, *J. Am. Chem. Soc.*, **83**, 1852 (1961).

(17) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-metallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, p. 1228 ff.

(18) All melting points and boiling points are uncorrected.

dried over anhydrous magnesium sulfate, and evaporated to dryness giving a red, oily residue, with a strong e.s.r. signal. On standing, a solid separated from this residue and was recrystallized from hexane to constant m.p. 115–117°, 3.0 g. The infrared spectrum of this compound showed the presence of phenyl (705 s, 780 s, 1600 m cm.<sup>-1</sup>), *t*-butyl (1205 s, 1370 s, 1395 m cm.<sup>-1</sup>), and NH or OH [3220 s cm.<sup>-1</sup> (broad)] groups. Its n.m.r. spectrum in CCl<sub>4</sub>, singlet at 8.98 (*t*-butyl), singlet at 2.87 (phenyl), and a broad singlet at 1.79  $\tau$  (NH or OH) in the ratio 5:9:1, was consistent with its formulation as either N-*t*-butylaniline or N-*t*-butyl-N-phenylhydroxylamine. The compound formed a hydrochloride on passing anhydrous hydrogen chloride into its ethereal solution which analyzed for N-*t*-butyl-N-phenylhydroxylammonium chloride, m.p. 131–132.5°.

*Anal.* Calcd. for C<sub>16</sub>H<sub>18</sub>NOCl: C, 59.54; H, 8.00; N, 6.95; Cl, 17.58. Found: C, 59.72; H, 7.79; N, 7.30; Cl, 17.49.

Attempted distillation of a portion of the residue from which N-*t*-butyl-N-phenylhydroxylamine had crystallized led to extensive decomposition, but a small amount of red liquid, b.p. 36–50° (1 mm.), could be isolated. Its infrared spectrum showed bands at 700 m, 750 s, and 1605 s cm.<sup>-1</sup> (phenyl); 1225 s, 1370 ms, 1395 m cm.<sup>-1</sup> (*t*-butyl); and 3380 w cm.<sup>-1</sup> (NH or OH); and is consistent with its formulation as N-*t*-butylaniline, which e.s.r. showed to be contaminated by di-*t*-butylnitroxide. This assignment was confirmed by conversion to its hydrochloride, m.p. 231–232°. The n.m.r. spectrum of this hydrochloride in CDCl<sub>3</sub> was consistent with the proposed structure. Peaks at 8.75 2.52, and -1.13  $\tau$  in the ratio 9.0:5.15:1.76 were observed, corresponding to one *t*-butyl, one phenyl, and one -NH<sub>2</sub> group. The peak at -1.13 disappeared in D<sub>2</sub>O as expected for exchangeable protons.

*Anal.* Calcd. for C<sub>16</sub>H<sub>18</sub>NCl: C, 64.68; H, 8.69; N, 7.54; Cl, 19.09. Found: C, 64.69; H, 8.70; N, 8.76; Cl, 19.39.

Attempts to isolate pure *t*-butylphenylnitroxide by column chromatography were unsuccessful owing to its decomposition. Removal of impurities by short path distillation at 75° (0.02 mm.) left *t*-butylphenylnitroxide (identified by e.s.r.) in a purity of 50% in the residue as calculated from its observed molar magnetic susceptibility,  $520 \times 10^{-6}$  c.g.s. unit. Oxidation of a 10% pentane solution of N-*t*-butyl-N-phenylhydroxylamine with silver oxide gave, after evaporation of the solvent *in vacuo*, a dark red liquid. Its observed molar magnetic susceptibility,  $885 \times 10^{-6}$  c.g.s. unit, corresponds to a calculated purity of 79% for *t*-butylphenylnitroxide. The infrared spectrum of this impure product, which showed phenyl (700 s, 760 s, 1590 w cm.<sup>-1</sup>) and *t*-butyl (1195 s, 1360 ms, 1400 mw cm.<sup>-1</sup>) bands but no NH or OH bands in the 3000–3500 cm.<sup>-1</sup> region, was consistent with its formulation as *t*-butylphenylnitroxide. Further confirmation for this structure is provided by its e.s.r. spectrum, taken in benzene, which consisted of three equally spaced lines of equal intensity which had an h.c.c. of 12.50 gauss. These lines are attributed to interaction of the unpaired electron with a nitrogen nucleus. At high dilution, after degassing, each of these lines is further split into nine lines with a ratio of intensities 1:2:4:6:6:6:4:2:1, attributed to interaction with one set of three equivalent protons (*ortho* and *para*) and one set of two equivalent protons (*meta*) whose h.c.c.'s are in the ratio 2:1. The h.c.c.'s were measured as  $a_o = a_p = 2a_m = 1.82$  gauss.

*t*-Butylphenylnitroxide appears to be quite unstable at room temperature in bulk because within 16 hr. after obtaining the sample which was 79% pure, the observed susceptibility dropped to  $465 \times 10^{-6}$  c.g.s. units, indicating 45% purity. The decomposition product appears to be an organic nitrate, as shown by the bands at 1625 s, 1270 m, and 860 m cm.<sup>-1</sup> in the infrared spectrum of the decomposing nitroxide. This material was also found as an impurity in a sample of the *t*-butylphenylnitroxide collected by v.p.c. In dilute solutions sealed under vacuum, *t*-butylphenylnitroxide is much more stable since the e.s.r. spectrum of the solutions used to measure the proton h.c.c.'s did not change for several months.<sup>18a</sup>

With the known compounds in hand for use as standards, the original reaction mixture was then re-analyzed by a variety of methods. The results together with the method of analysis used are listed in Table II.

**Reaction of Phenyllithium with *t*-Nitrobenzene.**—To a solution of phenyllithium, prepared from 7 g. (1 g.-atom) of lithium and 78 g. (0.5 mole) of bromobenzene in 380 ml. of ether, was added 50 g. (0.485 mole) of *t*-nitrobenzene dissolved in an equal volume of ether. The reaction mixture was cooled to -78° during addition, since addition of the nitro compound at room temperature was accompanied by a vigorous exotherm making the reaction difficult to control. After addition was complete, the reaction mixture was allowed to warm slowly to room temperature and sit for 2 days prior to hydrolysis. After hydrolysis, the

(18a) NOTE ADDED IN PROOF.—Crude solutions of *t*-butylphenylnitroxide have recently been prepared by the reaction of phenyl Grignard reagent with *t*-nitrobenzene (H. Wemair, A. Rassat, and A. M. Ravet, *Bull. Soc. Chim. France*, 1980 (1963)).

TABLE II  
PRODUCTS FROM THE REACTION OF PHENYLSODIUM WITH  
*t*-NITROBUTANE AFTER HYDROLYSIS

Product	Mole	Yield, %	Method of analysis
$\begin{array}{c} \text{O} \\   \\ \text{C}_6\text{H}_5\text{N}-t\text{-C}_4\text{H}_9 \\   \\ \text{OH} \end{array}$	0.152	30.4	E.s.r., v.p.c.
$\text{C}_6\text{H}_5\text{N}-t\text{-C}_4\text{H}_9$	0.018	3.6	V.p.c., isolation
$\text{C}_6\text{H}_5\text{NH}-t\text{-C}_4\text{H}_9$	.076	15.2	V.p.c., infrared
$t\text{-C}_4\text{H}_9\text{NO}_2$	.049	9.8	Infrared
$t\text{-C}_4\text{H}_9\text{N}=\text{O}$	.055	11.0	V.p.c.
$(t\text{-C}_4\text{H}_9)_2\text{N}-\text{O}$	Trace		V.p.c., e.s.r.
$\text{NaNO}_2$	0.005	1.0	Titrimetric assay

dark red ether layer was assayed by e.s.r. and found to contain *t*-butylphenyl nitroxide, 75 mmoles, in a yield of 15%.

**Reaction of *t*-Butyllithium with *t*-Nitrobutane.**—A solution of *t*-butyllithium in 300 ml. of ether was prepared, essentially by the procedure of Bartlett,<sup>19</sup> from *t*-butyl chloride (46.5 g., 0.5 mole) and 7.50 g. (1.08 g.-atoms) of lithium metal (as a 15% dispersion in mineral oil) containing 2% of sodium. To this solution 50 g. (0.485 mole) of *t*-nitrobutane was added dropwise with stirring over the course of several hours, while maintaining the reaction mixture at  $-40^\circ$ . If addition of the nitro compound became too rapid, the temperature rose rapidly to  $-25^\circ$ . After addition was completed, the reaction mixture was allowed to warm to room temperature and sit overnight. At the end of this time it was cooled to  $0^\circ$  and hydrolyzed by the addition of 125 ml. of water to give a greenish ether layer and a colorless aqueous layer. Analysis by v.p.c. showed that isobutylene, *t*-butyl alcohol, *t*-nitrobutane, di-*t*-butylnitroxide, and tri-*t*-butylhydroxylamine were present. The amount of each constituent was 13.3, 0.03, 21.9, 5.95, and 0.136 g., respectively, corresponding to a di-*t*-butylnitroxide yield of 15.1% based on unrecovered *t*-nitrobutane.

***t*-Butyl-2,6-dimethoxyphenyl nitroxide (IIc).**—2,6-Dimethoxyphenyllithium was prepared by the procedure of Wittig<sup>4</sup> from 52 g. (0.376 mole) of 1,3-dimethoxybenzene and 400 ml. of ether containing 0.376 mole of phenyllithium. To the stirred suspension of 2,6-dimethoxyphenyllithium, cooled in an ice bath, was added, under nitrogen over the course of 15 min., 41.5 g. (0.38 mole) of *t*-nitrobutane. Addition of the nitro compound was accompanied by the precipitation of colorless solid. On warming to room temperature, a slight exotherm occurred with gentle reflux of the ether. The reaction mixture was stirred for 7 hr. and allowed to stand for 1 day. It was then hydrolyzed with 200 ml. of water to give a red ether solution containing a suspended solid. The solid was identified as the lithium salt of 2,6-dimethoxyphenol by conversion of the salt to the phenol, m.p. 51–52, reported<sup>20</sup> m.p. 54–55°, and by its infrared spectrum which was consistent with this structure. The corresponding picrate had m.p. 68–69°, reported<sup>20</sup> m.p. 61°. The solvent was distilled from the filtrate *in vacuo* leaving a red, oily residue. After the addition of pentane, colorless crystals formed, 15.8 g., which were filtered and recrystallized once from methanol and once from cyclohexane to give platelets, m.p. 126–127°. This product had an infrared spectrum and analysis consistent with N-*t*-butyl-N-(2,6-dimethoxyphenyl)-hydroxylamine.

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{19}\text{O}_3\text{N}$ : C, 63.97; H, 8.50; N, 6.22. Found: C, 63.86; H, 8.06; N, 6.36.

The pentane solution, from which hydroxylamine had been removed, was evaporated and the residual oil molecularly distilled at  $70\text{--}80^\circ$  (1 mm.). The distillate, consisting mainly of recovered 2,6-dimethoxybenzene, had an e.s.r. signal due to *t*-butyl-2,6-dimethoxyphenyl nitroxide, but the larger h.c.c. of di-*t*-butylnitroxide was absent. The residue crystallized on standing and could be recrystallized from cyclohexane or sublimed to give orange platelets of *t*-butyl-2,6-dimethoxyphenyl nitroxide; 15.0 g., 17.8%, m.p. 101–102.5°; effective magnetic moment, 1.73 B.M. (theor. 1.73). The e.s.r. spectrum of pure *t*-butyl-2,6-dimethoxyphenyl nitroxide showed a single line with a peak to peak line width of 11.6 gauss and a *g*-value of 2.0062. In dilute benzene solution the spectrum consisted of three equally spaced lines of equal intensity with an h.c.c. of 13.22 gauss.

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{16}\text{NO}_3$ : C, 64.24; H, 8.09; N, 6.23. Found: C, 64.24; H, 8.05; N, 6.41.

***t*-Cumyl-2,6-dimethoxyphenyl nitroxide (IIId).**—A slurry of 0.5 mole of 2,6-dimethoxyphenyllithium in 500 ml. of anhydrous ether was stirred at  $0^\circ$  under nitrogen while 40 g. (0.242 mole) of 2-nitro-2-phenylpropane in 150 ml. of ether was added over the

course of 0.5 hr. After stirring the mixture at  $0^\circ$  for 1 hr., the ice bath was removed and the mixture allowed to reach room temperature. After several hours, the reaction mixture was hydrolyzed with 200 ml. of water. A solid precipitated and the organic layer turned red. The layers were separated and the aqueous layer containing the suspended solid was filtered. The solid, 25 g., was identified by its infrared spectrum as the lithium salt of 2,6-dimethoxyphenol.

The ethereal layer was washed with water, dried over anhydrous magnesium sulfate, and the solvent evaporated *in vacuo* at room temperature. Unreacted 2,6-dimethoxybenzene and 2-nitro-2-phenylpropane were removed from the residue by molecular distillation at  $50\text{--}55^\circ$  (1 mm.). The oily residue was extracted several times with boiling petroleum ether, b.p.  $30\text{--}60^\circ$ . Upon cooling, the solution deposited large crystals of *t*-cumyl-2,6-dimethoxyphenyl nitroxide. After two recrystallizations from petroleum ether it was obtained as shining amber needles, m.p.  $77\text{--}78^\circ$ , 8.15 g., 11.8%; effective magnetic moment 1.74 B.M. (theor. 1.73). The e.s.r. spectrum of the pure solid was a single line with a peak to peak line width of 8.8 gauss and a *g*-value of 2.0060. The h.c.c. to the nitrogen atom was 13.19 gauss in dilute benzene solution. In a separate experiment employing 0.07 mole of *t*-nitrobenzene and 1 equivalent of 2,6-dimethoxyphenyllithium, bicumyl was detected by v.p.c. in a yield of 0.18 g., 2.0%. Sodium nitrite, 0.002 mole, was also found in a yield of 2.9%.

*Anal.* Calcd. for  $\text{C}_{17}\text{H}_{20}\text{NO}_2$ : C, 71.28; H, 7.07; N, 4.89. Found: C, 71.46; H, 6.91; N, 4.81.

**Bis-(2,6-dimethoxyphenyl)-nitroxide (IIe).**—A suspension of 0.3 mole of 2,6-dimethoxyphenyllithium in 200 ml. of ether was treated with a slurry of 50 g. (0.27 mole) of 2,6-dimethoxynitrobenzene<sup>21</sup> in 600 ml. of 1:1 ether-benzene solution. The reaction mixture was maintained at  $15\text{--}18^\circ$  during the addition of the nitro compound. After addition was complete, the solution began to warm up with refluxing of the ether. The reaction mixture was immersed in an ice bath to control the exotherm. After stirring for 1 hr., it was allowed to warm to room temperature and stirred for an additional 7 hr. At the end of this time the reaction mixture consisted of a steel blue solid and a clear brown supernatant. The bulk of the supernatant layer was withdrawn and the residual solid washed with two successive 200-ml. portions of ether and finally hydrolyzed by the addition of 100 ml. of water to give a scarlet solid. All operations up to this point were conducted under nitrogen. The hydrolysate was filtered and the solid washed with small portions of water, ether and, finally, with 100 ml. of ice-cold acetone. The crude product was recrystallized from acetone to give 4.3 g. of crude bis-(2,6-dimethoxyphenyl)-nitroxide as brilliant red plates. Recrystallization from methanol gave an analytical sample, 3.5 g., 4.2%, sintering at  $190^\circ$ , m.p.  $199\text{--}200^\circ$  dec.; effective magnetic moment 1.74 B.M. (theor. 1.73 B.M.). The e.s.r. spectrum of the pure solid consisted of a single line with a peak to peak width of 6.6 gauss and a *g*-value of 2.0067. The h.c.c. to the nitrogen atom was found to be 10.17 gauss in dilute benzene solution.

*Anal.* Calcd. for  $\text{C}_{16}\text{H}_{16}\text{NO}_2$ : C, 63.15; H, 5.96; N, 4.60. Found: C, 63.42; H, 6.10; N, 4.39.

**2,4',6'-Trimethoxydiphenyl nitroxide (IIIf).**<sup>21a</sup>—*p*-Nitroanisole (77 g., 0.50 mole), diluted with 250 cc. of ether, was added dropwise to 0.5 mole of ethereal 2,6-dimethoxyphenyllithium cooled in an ice bath. After stirring for 0.5 hr., the mixture was hydrolyzed with 200 ml. of water to give a three-phase system: an ether layer, an aqueous layer, and a solid. The solid was filtered, the layers were separated, and the organic layer, combined with three ethereal extracts of the aqueous phase, was dried over magnesium sulfate.

The cream colored solid turned red on standing in air. It was exhaustively extracted with hot ether to leave the lithium salt of 2,6-dimethoxyphenol. Concentration of the ether extract followed by cooling in ice gave 3 g. of crude, orange 2,4',6'-trimethoxydiphenyl nitroxide, m.p.  $111\text{--}114^\circ$ , in a purity of 59% established by its molar magnetic susceptibility. An analytical sample, 0.35 g., m.p.  $114.5\text{--}115^\circ$ , was obtained after four recrystallizations from ether. The amount of purified sample was too small to determine its effective magnetic moment. Its e.s.r. spectrum showed a single line slightly asymmetric with a peak to peak line width of 10.0 gauss and a *g*-value of 2.0055. The h.c.c. to the nitrogen atom was found to be 10.10 gauss. Displacement of the air in the sample by nitrogen revealed further splitting by two equivalent protons with an h.c.c. of 2.61 gauss.

*Anal.* Calcd. for  $\text{C}_{15}\text{H}_{16}\text{NO}_4$ : C, 65.68; H, 5.88; N, 5.11; O, 23.33. Found: C, 65.62; H, 5.70; N, 5.39; O, 23.30.

Ether from the original organic layer was distilled *in vacuo* to give 120 g. of an oily residue. This was analyzed by e.s.r. and contained 0.078 mole of nitroxide or a total yield of 15%. All attempts to isolate crystalline nitroxide from this mixture failed.

(19) P. D. Bartlett and E. B. Lefferts, *J. Am. Chem. Soc.*, **77**, 2804 (1955).

(20) C. Graebe and H. Hess, *Ann.*, **340**, 232 (1905).

(21) A. Baeyer, *ibid.*, **372**, 80 (1909).

(21a) This experiment added Sept. 7, 1963.

**Reaction of Cumylpotassium with *t*-Nitrocumene.**—Cumylpotassium was prepared by the method of Morton<sup>22</sup> from 7.8 g. (0.20 g.-atom) of potassium sand, 24.0 g. (0.20 mole) of cumene, and 10.6 g. (0.10 mole) of 1-chloropentane in 75 ml. of heptane. *t*-Nitrocumene (16.8 g., 0.10 mole) was added with stirring to the deep red cumylpotassium solution while maintaining the temperature at  $-10$  to  $-5^\circ$  during its addition. Stirring at this temperature was continued for 1 hr. after the addition was completed. *t*-Butyl alcohol, 20 ml., was then added to destroy any excess potassium. The solution was filtered to give 16.0 g. of colorless solid which assayed for a mixture of 7.25 g. of potassium chloride and 9.20 g. of potassium nitrite, in yields of 97 and 107%, respectively. The filtrate, 79.0 g., contained  $2.6 \times 10^{-4}$  mole of di-*t*-cumylnitroxide having a nitrogen h.c.c. of 14.9 gauss. Analysis of the filtrate by v.p.c. showed the presence of bicumyl (7.6 g., 42% yield based on reacted *t*-nitrocumene),  $\alpha$ -methylstyrene (0.9 g.), cumene (13.3 g.), *t*-nitrocumene (4.0 g.), and four unidentified components (combined weight, 1.9 g.) which were not further investigated.

**Reaction of Cumylpotassium with *t*-Nitrobutane.**<sup>23a</sup>—*t*-Nitrobutane (10.2 g., 0.10 mole) was added to 0.10 mole of cumylpotassium in 75 ml. of heptane at  $-15^\circ$  over a period of 1 hr. After stirring for 0.5 hr., the reaction mixture was allowed to warm to room temperature and *t*-butyl alcohol (20 ml.) was added to destroy excess potassium. The mixture was hydrolyzed with 100 ml. of water, extracted with ether, and the extract dried over magnesium sulfate. Evaporation of the solvent *in vacuo* resulted in the loss of *t*-nitrosobutane and left a red oily residue which was analyzed by v.p.c. Among the 22 components detected, heptane (5.08 g.), *t*-nitrobutane (0.091 g.), cumene (13.8 g.), di-*t*-butylnitroxide (0.585 g.), tri-*t*-butylhydroxylamine (1.99 g.), and bicumyl (0.461 g.) were identified by their retention times relative to *o*-dichlorobenzene. The remaining components, ranging in amount from 0.030 to 0.390 g., were not further investigated.

(22) A. A. Morton and E. J. Lanpher, *J. Org. Chem.*, **23**, 1636 (1958).

**Reaction of *t*-Butylmagnesium Chloride with *t*-Nitrobutane.**—*t*-Nitrobutane (50.0 g., 0.485 mole), dissolved in an equal volume of ether, was added to the Grignard reagent prepared from 46.5 g. (0.5 mole) of *t*-butyl chloride and 12.2 g. (0.5 mole) of magnesium. The Grignard solution was cooled to  $-78^\circ$  prior to the addition of the nitro compound. During its addition, over the course of 1 hr., the reaction mixture turned green and a solid precipitated. The reaction mixture was stirred at  $25^\circ$  for 0.5 hr. after which it was hydrolyzed by the addition of water at  $0^\circ$ . Hydrolysis was accompanied by the evolution of isobutylene. The organic layer was separated and dried over anhydrous magnesium sulfate. Analysis by e.s.r. showed it to contain about  $10^{-2}$  mole of di-*t*-butylnitroxide. Other products, identified by v.p.c., were *t*-nitrosobutane, *t*-butyl alcohol, *t*-butyl nitrate, and tri-*t*-butylhydroxylamine.

***p,p'*-Dianisylnitroxide.**—The Grignard reagent was prepared from *p*-bromoanisole (61 g., 0.326 mole) and 8.7 g. (0.358 mole) of magnesium in 1 l. of 1:1 ether-benzene by the procedure of Reid.<sup>23</sup> It was cooled in ice and *p*-nitroanisole (42.4 g., 0.326 mole) was added over a 1-hr. period. At the end of this time 200 ml. of water was added slowly until the magnesium salts had coagulated. The organic layer was decanted from the magnesium salts and evaporatively distilled at  $30^\circ$ . The residue showed a typical nitroxide e.s.r. signal. All attempts at purification, however, failed. Small amounts of di-*p*-anisyl and di-*p*-anisylamine were shown to be present in this residue by comparison of its infrared spectrum with those of authentic samples.

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(23) J. C. Reid and H. B. Jones, *J. Biol. Chem.*, **174**, 427 (1948).

[CONTRIBUTION FROM THE U. S. ARMY BALLISTICS RESEARCH LABORATORIES, ABERDEEN PROVING GROUNDS, MD.; FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, PRINCETON, N. J.; AND THE UNIVERSITY OF LUND, LUND, SWEDEN]

## Conformational Effects and Hydrogen Bonding in 1,4-Diols<sup>1</sup>

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Study of the influence of conformation and configuration on intramolecular hydrogen bonding in diols has been extended to 1,4-dihydroxybutane derivatives. The 3  $\mu$  infrared spectra of 57 butane-1,4-diols substituted only upon the 2- and 3-positions—acyclic, unsaturated, monocyclic, and bicyclic examples—were examined in detail. In a formal sense these 1,4-diols resemble the 1,2-diols studied earlier by similar techniques, the  $-\text{CH}_2\text{OH}$  groups of 1,4-diols replacing the  $-\text{OH}$  groups of 1,2-diols; however, the two series of compounds behave quite differently. In 1,2-diols the spectral shifts ( $\Delta\nu$ ) due to intramolecular hydrogen bonding decrease with increasing azimuthal angle between OH groups, but the reverse is true for 1,4-diols. A maximum  $\Delta\nu$  appears to be reached when the azimuthal angle between adjacent  $\text{CH}_2\text{OH}$  groups in 1,4-diols is about  $90^\circ$ . A conformational analysis of 1,4-diols with different azimuthal angles provides an explanation for this behavior; optimum hydrogen bonding interactions can be achieved only in certain geometrical arrangements. Evidence is presented that more than one major conformation permitting hydrogen bonding is present in certain of the diols. The influence of other structural variations on spectral details is discussed.

Intramolecular hydrogen bonding is particularly sensitive to changes in molecular geometry. For 1,2-diols, the most extensively studied class of compounds, the magnitude of the infrared spectral shifts ( $\Delta\nu$ ) of the fundamental OH stretching vibrational bands due to intramolecular association have been correlated with configurational and conformational factors.<sup>6-8</sup> In 1,2-

diols, the azimuthal angle,  $\phi$ , between two C—O bonds on adjacent carbon atoms is of prime importance in determining  $\Delta\nu$ <sup>3,9</sup>; values ranging from  $\Delta\nu = 0 \text{ cm.}^{-1}$  for compounds where the hydroxyl groups are too far apart to permit intramolecular interaction (e.g., *trans*-cyclopentane-1,2-diol,  $90^\circ < \phi < 120^\circ$ )<sup>6,9</sup> to  $\Delta\nu = 103 \text{ cm.}^{-1}$  (*cis*-*exo*-norbornane-2,3-diol,  $\phi = 0^\circ$ )<sup>10,11</sup> have been reported (Table II). Most 1,2-diols have  $\phi$  azi-

(1) Presented at the Fourth Delaware Valley Regional Meeting, American Chemical Society, Philadelphia, Pa., Jan., 1962. Abstracts, p. 77, and at the Ninth Conference on Reaction Mechanisms, Brookhaven, N. Y., Sept., 1962.

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(5) University of Lund.

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(11) Even though  $\phi \cong 0^\circ$  in *cis*-cyclobutane-1,2-diols,  $\Delta\nu \cong 65 \text{ cm.}^{-1}$  because of the greater OH...O distance caused by distortion of the C—C—C ring angles to  $90^\circ$ : R. Criegee and K. Noll, *Ann.*, **627**, 1 (1959); E. J. Moriconi, W. F. O'Connor, L. P. Kuhn, E. A. Keneally, and F. T. Wallenberger, *J. Am. Chem. Soc.*, **81**, 6472 (1959). See Table IV.