

correspond to the half-wave potential of the reduction wave. For electrolyses in glyme, tetra-*n*-butylammonium perchlorate was the supporting electrolyte. No reference electrode was used for glyme solutions, but the voltage was increased slowly until a threshold current of 2  $\mu$ a. was passed through the cell. Observations were also made with voltages such that 10 and 20  $\mu$ a. were also passed. Although no reference electrode was used, the relatively high concentrations of nitro compounds (all were 10 mM), the similarity of results to those obtained for acetonitrile and the low currents passed make it likely that the generating conditions in glyme were near the initial portion of the reduction wave.

At the outset of *t*-nitrobutane reduction in acetonitrile, five lines appeared similar to those in Fig. 4a. On discontinuing the electrolysis the two outside lines spaced 26.4 gauss from the center faded rapidly while the two lines spaced 15.7 gauss from the center grew in intensity and the entire spectrum became similar to that shown in Fig. 4b. This remaining spectrum, which underwent no further change, is due to di-*t*-butylnitroxide. The original spectrum, therefore, is comprised of two sets of triplets each consisting of three equally spaced lines of equal intensity whose center lines are superimposed. The triplet with a hyperfine coupling constant (h.c.c.) of 26.4 gauss is due to the *t*-nitrobutyl anion radical whose spectrum in glyme is shown in Fig. 3.

Electrolysis of *t*-nitrobutane in glyme showed at the 2- $\mu$ a. level and more clearly at the 10- or 20- $\mu$ a. level, Fig. 4a, that the same two paramagnetic species were produced as were observed in acetonitrile. The corresponding h.c.c.'s are slightly decreased in

glyme, being 26.2 and 15.4 gauss for the *t*-nitrobutyl anion radical and di-*t*-butylnitroxide, respectively. Such changes in h.c.c. with change in solvent are not uncommon.<sup>48,49</sup> The anion radical of *t*-nitrobutane is also unstable in glyme since on discontinuing electrolysis the spectrum of the anion radical disappeared rapidly leaving only the spectrum of di-*t*-butylnitroxide, Fig. 4b, which increased in intensity. When fresh glyme solutions of *t*-nitrobutane (less than 10 mM) were electrolyzed at currents somewhat higher than 20  $\mu$ a., only the *t*-nitrobutyl anion radical was visible for a short period of time at the outset of electrolysis as shown in Fig. 3. After stopping the electrolysis, its spectrum was rapidly replaced by that of di-*t*-butylnitroxide. The decay of the *t*-nitrobutyl anion radical after stopping electrolysis was recorded by photographing the decrease in its e.s.r. spectrum from the screen of an oscilloscope with a calibrated time base. The spectrum of such a solution, if electrolysis was continued, showed the coexistence of the *t*-nitrobutyl anion radical with di-*t*-butylnitroxide while current was being passed as seen in Fig. 4a.

**Acknowledgments.**—The authors are indebted to Mr. A. M. Feldman for his help with some of the experiments and to Mr. E. S. Everett for v.p.c. analyses. They also wish to thank Dr. G. W. Kennerly for his continued encouragement throughout the course of this work.

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## Mechanism of the Formation of Di-*t*-butylnitroxide from *t*-Nitrobutane and Sodium Metal

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RECEIVED APRIL 20, 1963

The reaction of metallic sodium with *t*-nitrobutane in 1,2-dimethoxyethane has been studied. A mechanism for the formation of di-*t*-butylnitroxide and other products of the reaction is proposed. It involves the reaction of a *t*-butyl radical derived from the collapse of a *t*-nitrobutyl anion radical with additional *t*-nitrobutyl anion radical to form a diamagnetic salt,  $(t-C_4H_9)_2NO_2 \cdot Na^+$ . This salt upon hydrolysis produces di-*t*-butylnitroxide. A salt of this type can also be derived from the interaction of phenylsodium with *t*-nitrobutane which, after hydrolysis, affords *t*-butylphenylnitroxide.

### Introduction

A preliminary account of the reaction of *t*-nitrobutane with sodium to form the stable free radical di-*t*-butylnitroxide has been given.<sup>1,2</sup> Subsequent work designed to determine the scope of this unusual reaction has established that substantial yields of nitroxides are not obtained from nitro compounds other than *t*-nitrobutane. In the previous paper<sup>3</sup> the reactions of several tertiary nitro anion radicals were described. Each anion radical was shown to undergo scission to nitrite ion and the corresponding free radical. Subsequent to their formation, these free radicals disproportionate and dimerize. The anion radical of *t*-nitrobutane, however, yields a variety of products not analogous to those obtained from the other nitro compounds. The unique behavior of *t*-nitrobutane has been attributed to the relatively long lifetime of its anion radical which permits it to scavenge the *t*-butyl radicals it generates. Among the products formed in this reaction is a reactive solid which is instantly hydrolyzed to di-*t*-butylnitroxide and other products. The constitution of the reaction products, the reactions by which they are formed, and the route by which di-*t*-butylnitroxide arises comprise the subject of this paper.

(1) A. K. Hoffmann and A. T. Henderson, *J. Am. Chem. Soc.*, **83**, 4671 (1961).

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### Results

After complete reaction of 1 gram equivalent of sodium with *t*-nitrobutane in glyme, the initially lavender mixture (known to contain *t*-nitrobutane anion radicals) consists of two phases: a colorless supernatant solution and a colorless diamagnetic solid. For a typical run, the products found in the supernatant solution after removal of the solid are listed in Table I. It is

TABLE I<sup>a</sup>  
PRODUCTS FOUND IN THE SUPERNATANT PHASE FROM THE REACTION OF *t*-NITROBUTANE WITH ONE EQUIVALENT OF SODIUM

| Product  | Run I, mmoles | Run II, mmoles |
|--|---------------|----------------|
| <i>i</i> -C <sub>4</sub> H <sub>8</sub> <sup>b</sup>     | 12.0          | 7.8            |
| <i>t</i> -C <sub>4</sub> H <sub>9</sub> OH               | 3.8           | 2.2            |
| <i>t</i> -C <sub>4</sub> H <sub>9</sub> ONO <sub>2</sub> | 3.7           | 2.3            |
| <i>t</i> -C <sub>4</sub> H <sub>9</sub> NO <sub>2</sub>  | 13.5          | 17.6           |
| $(t-C_4H_9)_2NO-t-C_4H_9$                                | 18.8          | 12.7           |
| $(t-C_4H_9)_2N \cdot O$                                  | <sup>c</sup>  | <sup>c</sup>   |
| <i>t</i> -C <sub>4</sub> H <sub>9</sub> NH <sub>2</sub>  | <sup>d</sup>  | <sup>d</sup>   |

<sup>a</sup> In these runs 390 mmoles of *t*-nitrobutane was used. <sup>b</sup> Some loss may have been incurred due to a slow nitrogen sweep during filtration. The values reported for isobutylene include roughly 10% of isobutane which was not resolved from isobutylene under the conditions of the v.p.c. analyses. <sup>c</sup> E.s.r. assays showed concentrations of di-*t*-butylnitroxide of approximately 0.06 mmole. <sup>d</sup> Small amounts of *t*-butylamine were isolated as the hydrochloride.

seen that these products account for only a relatively small proportion, roughly 20 mole % of the starting *t*-butyl groups or 13% of the total reactant weight.

TABLE II

PRODUCTS FROM HYDROLYSIS OF THE SOLID PHASE DERIVED FROM THE REACTION OF *t*-NITROBUTANE WITH ONE EQUIVALENT OF SODIUM

| Product  | In glyme           |                |                    |                | In heptane         |                |                    |                | In glyme <sup>b</sup> with <i>p</i> -nitroso-dimethylaniline |                |
|--|--------------------|----------------|--------------------|----------------|--------------------|----------------|--------------------|----------------|--|----------------|
|  | Run 1 <sup>a</sup> |                | Run 2 <sup>a</sup> |                | Run 3 <sup>a</sup> |                | Run 4 <sup>a</sup> |                | mmoles per   |                |
|  | 10 g. of solid     | Wt. % of solid | 10 g. of solid     | Wt. % of solid | 10 g. of solid     | Wt. % of solid | 10 g. of solid     | Wt. % of solid | 10 g. of solid   | Wt. % of solid |
| <i>i</i> -C <sub>4</sub> H <sub>8</sub>                      | 2.9                | 1.6            | 2.8                | 1.6            | 3.3                | 1.8            | 3.7                | 2.1            | 2.0  | 1.1            |
| <i>t</i> -C <sub>4</sub> H <sub>9</sub> NO                   | 6.8                | 5.9            | 7.2                | 6.3            | 22.1               | 19.2           | 21.4               | 18.6           | 4.5  | 3.9            |
| <i>t</i> -C <sub>4</sub> H <sub>9</sub> OH                   | 3.5                | 2.6            | 4.3                | 3.2            | 7.7                | 5.7            | 6.6                | 4.9            | 1.2  | 0.9            |
| <i>t</i> -C <sub>4</sub> H <sub>9</sub> NO <sub>2</sub>      | 1.8                | 1.9            | 1.5                | 1.5            | 1.5                | 1.6            | 2.2                | 2.3            | ..   | ..             |
| ( <i>t</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> N-O | 25.4               | 36.6           | 21.3               | 30.0           | 8.7                | 12.5           | 9.1                | 13.1           | 32.8   | 47.3           |
| NaNO <sub>2</sub>  | 45.4               | 31.3           | 38.0               | 26.2           | 37.8               | 26.1           | 40.0               | 27.6           | ..   | ..             |
| NaOH   | 33.0               | 13.2           | 38.7               | 15.5           | 32.2               | 12.9           | 38.5               | 15.4           | ..   | ..             |
| Total  |                    | 93.1           |                    | 84.4           |                    | 80.1           |                    | 84.2           |  |                |

<sup>a</sup> In runs 1, 2, 3, and 4, 5.3639, 5.5567, 5.5255, and 4.6025 g. were used, respectively. <sup>b</sup> Started with 5.8944 g. of solid.

By contrast, the solid phase accounted for 87–88% of the total reactant weight. The solid rapidly turned red on exposure to atmospheric moisture with the formation of di-*t*-butylnitroxide. It was rapidly decomposed by hydroxylic solvents such as alcohols or acetic acid to form di-*t*-butylnitroxide and was instantly hydrolyzed by water to give the products shown in Table II. Clearly, the bulk of the di-*t*-butylnitroxide is not formed directly as a primary reduction product of *t*-nitrobutane but results from the subsequent reaction of the solid with water. No effect on the products was observed if the solid and supernatant phases were not separated. Thus, if water was added to the total reaction mixture, the products were a combination of those found in the supernatant phase and those produced by the solid on hydrolysis as shown in Table III.

TABLE III

PRODUCTS FROM HYDROLYSIS OF TOTAL REACTION MIXTURES DERIVED FROM *t*-NITROBUTANE AND ONE EQUIVALENT OF SODIUM IN GLYME

| Product <sup>a</sup>   | Run 1 <sup>b</sup> |                                 | Run 2 <sup>c</sup> |                                 | Calcd. % |
|--|--------------------|---------------------------------|--------------------|---------------------------------|----------|
|  | %                  |                                 | %                  |                                 |          |
|  | mmoles             | starting <i>t</i> -butyl groups | mmoles             | starting <i>t</i> -butyl groups |          |
| <i>i</i> -C <sub>4</sub> H <sub>8</sub>  | 5.6                | 5.6                             | 9.6                | 6.6                             | 5.7      |
| <i>t</i> -C <sub>4</sub> H <sub>9</sub> NO   | 5.0                | 5.0                             | 4.1                | 2.8                             | 7.7      |
| <i>t</i> -C <sub>4</sub> H <sub>9</sub> OH   | 3.5                | 3.5                             | 1.2                | 0.8                             | 5.1      |
| <i>t</i> -C <sub>4</sub> H <sub>9</sub> ONO <sub>2</sub>   | 0.6                | 0.6                             | 1.5                | 1.0                             | 0.8      |
| <i>t</i> -C <sub>4</sub> H <sub>9</sub> NO <sub>2</sub>  | 8.2                | 8.2                             | 9.3                | 6.4                             | 5.9      |
| ( <i>t</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> N-O   | 23.9               | 47.8                            | 39.2               | 53.8                            | 51.2     |
| ( <i>t</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> NO- <i>t</i> -C <sub>4</sub> H <sub>9</sub> | 6.3                | 18.9                            | 7.6                | 15.6                            | 12.1     |
| ( <i>t</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> N-OH <sup>e</sup>                           | 1.3                | 2.6                             | 1.9                | 2.6                             | 2.6      |
| <i>t</i> -C <sub>4</sub> H <sub>9</sub> NHOH <sup>e</sup>  | 0.9                | 0.9                             | 1.3                | 0.9                             | 0.9      |
| <i>t</i> -C <sub>4</sub> H <sub>9</sub> -NHO- <i>t</i> -C <sub>4</sub> H <sub>9</sub> <sup>e</sup>   | 0.6                | 1.2                             | 0.9                | 1.2                             | 1.2      |
| Total  |                    | 94.3                            |                    | 91.7                            |          |

<sup>a</sup> Sodium nitrite was not determined for above runs. In numerous other runs of varying size, sodium nitrite accounted for 48–51% of the starting nitro groups. <sup>b</sup> Products from 100 mmoles of each reactant. <sup>c</sup> Products from 146 mmoles of each reactant. <sup>d</sup> Yields were calculated from average product values of runs 1 and 2 of Tables I and II. <sup>e</sup> *t*-Butylhydroxylamines were not assayed in these runs. The amounts reported are calculated from the results of larger scale runs.

**Constitution of the Solid.**—The constitution of the solid was of considerable interest since substantial amounts of di-*t*-butylnitroxide result only from its hydrolysis. The determination of its structure was hampered by insolubility in solvents with which it did not react and by the fact that it was not a single substance. X-Ray analysis showed it to contain approximately 30% by weight of sodium nitrite admixed with an organic solid. Since the solid contains all the starting sodium, the organic portion is presumed to be a salt. Because it was not found possible to purify this material, the total solid was employed in this

investigation although the structure of interest is that of the organic salt.

While moderately stable at room temperature, the solid decomposed at about 100° developing a pale lavender color, ultimately having a red cast if the decomposition was conducted in a sealed tube. The red color was due to di-*t*-butylnitroxide, as verified by e.s.r. During decomposition in the e.s.r. cavity no paramagnetic species other than di-*t*-butylnitroxide could be detected. When decomposition was effected at or above 100°, the major organic product was tri-*t*-butylhydroxylamine, Table IV.

TABLE IV

PRODUCTS FROM THE THERMAL DECOMPOSITION OF SOLID AT 140° (0.25 MM.)

| Product                   | <i>i</i> -C <sub>4</sub> H <sub>8</sub> <sup>a</sup>          | <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> ) <sub>2</sub> -NOH |
|---------------------------|---|---|--|---|
| mmoles per 10 g. of solid | 22.2  | 2.5   | 1.5  | 1.7   |
| Wt. % of starting solid   | 12.4  | 2.2   | 1.1  | 2.5   |
|                           | ( <i>t</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> -N-O | ( <i>t</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> -NO- <i>t</i> -C <sub>4</sub> H <sub>9</sub> | NaNO <sub>2</sub> <sup>b</sup>             | NaOH <sup>b</sup>   |
| mmoles per 10 g. of solid | 2.3   | 9.6   | 56.8                                       | 19.0  |
| Wt. % of starting solid   | 3.3   | 19.3  | 39.2                                       | 7.6   |

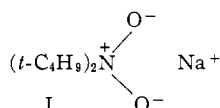
<sup>a</sup> Isobutane also present. <sup>b</sup> Nonvolatile residue.

The infrared spectrum of the solid, Fig. 1A, is relatively simple, showing the presence of inorganic nitrite, *t*-butyl groups, and a pattern of bands in the 900–1050 cm.<sup>-1</sup> region which can be attributed to the presence of N-O single bonds and *t*-butyl groups. Inorganic nitrite could be removed by triturating the solid with strong aqueous alkali. Although some decomposition occurred, the extracted solid had an infrared spectrum essentially unchanged except for the absence of nitrite bands; Fig. 1B. When hydrolyzed, solid thus treated retained its ability to form di-*t*-butylnitroxide but did not form any nitrite ion.

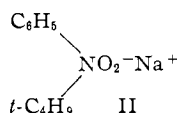
All attempts to prepare isolable derivatives of the salt failed. In each case di-*t*-butylnitroxide or products which are derived from its reaction with the added reagents were formed. Oxidative degradation by anhydrous iodine also led to di-*t*-butylnitroxide. Saturated aqueous sodium borohydride, however, in a mildly exothermic reaction smoothly converted the solid to N,N-di-*t*-butylhydroxylamine, and no di-*t*-butylnitroxide was formed. The hydroxylamine was produced in an amount comparable to the nitroxide which results from hydrolysis of the solid. Since di-*t*-butylnitroxide is inert to this reagent, it is concluded that two *t*-butyl groups are attached to the nitrogen atom of the organic salt in a structure resembling the sodium salt of N,N-di-*t*-butylhydroxylamine. This salt itself, however, cannot be present in the solid

because it is soluble in glyme and forms di-*t*-butylhydroxylamine on hydrolysis.

A reasonable, structurally similar organic salt is derived by combining a *t*-butyl radical with the *t*-nitrobutyl anion radical to form sodium *N,N*-di-*t*-butylhydroxylamine oxide (I).



Structures analogous to I have been postulated earlier<sup>4,5</sup> for complexes resulting<sup>6,7</sup> from the interaction of Grignard reagents with nitro compounds. If I, therefore, is a valid structural representation, then similar compounds should be obtainable from the reaction of anions with suitable nitro compounds. Thus, interaction of phenylsodium and *t*-nitrobutane should give an analogous salt, II, derived from the addition of an anion directly to the positively charged nitrogen atom of the nitro group.



In agreement with expectation, these reagents formed a colorless diamagnetic solid. Like solid obtained from *t*-nitrobutane, it was insoluble in solvents with which it did not react, it was unstable in the presence of atmospheric moisture, and it hydrolyzed instantly to give *t*-butylphenylnitroxide together with *N-t*-butylaniline and *N-t*-butyl-*N*-phenylhydroxylamine.<sup>8</sup> Its infrared spectrum, Fig. 1C, shows the presence of phenyl and *t*-butyl groups in the molecule. With the exception of a phenyl band at 1020  $\text{cm}^{-1}$ , a band pattern identical with that of the solid derived from *t*-nitrobutane and sodium is seen in the 900–1050  $\text{cm}^{-1}$  region. This finding strongly supports the assignment of structure I to the organic salt derived from *t*-nitrobutane and sodium. As shown elsewhere,<sup>8</sup> the conversion of *t*-nitrobutane by phenylsodium to II opens a convenient synthetic route to a variety of other nitroxides.

### Discussion

The first-order rate of decay of the *t*-nitrobutyl anion radical coupled with the formation of nitrite ion provides strong evidence for the decomposition of the anion radical into a *t*-butyl radical and nitrite ion<sup>3</sup> (1). From the structure of I it is evident that a *t*-butyl

$$\text{t-C}_4\text{H}_9\text{NO}_2 + e^- \longrightarrow \text{t-C}_4\text{H}_9\text{NO}_2^{\cdot-} \longrightarrow \text{t-C}_4\text{H}_9\cdot + \text{NO}_2^- \quad (1)$$

group must, in some manner, add to *t*-nitrobutane. Since *t*-butyl anions are not significant products of the reaction of sodium with *t*-nitrobutane,<sup>3</sup> it is reasonably concluded that reaction between *t*-butyl radicals and *t*-nitrobutyl anion radicals occurs. The products isolated indicate that in addition to combination (2), the *t*-butyl radical and the *t*-nitrobutyl anion radical undergo two additional reactions, hydrogen transfer (3) and oxygen abstraction (4). The efficiency of these reactions is indicated by the isolation of only 50% of the starting nitro groups as sodium nitrite and the incorporation of the remaining nitrogen into organic products. This implies that the *t*-nitrobutyl anion radical scav-

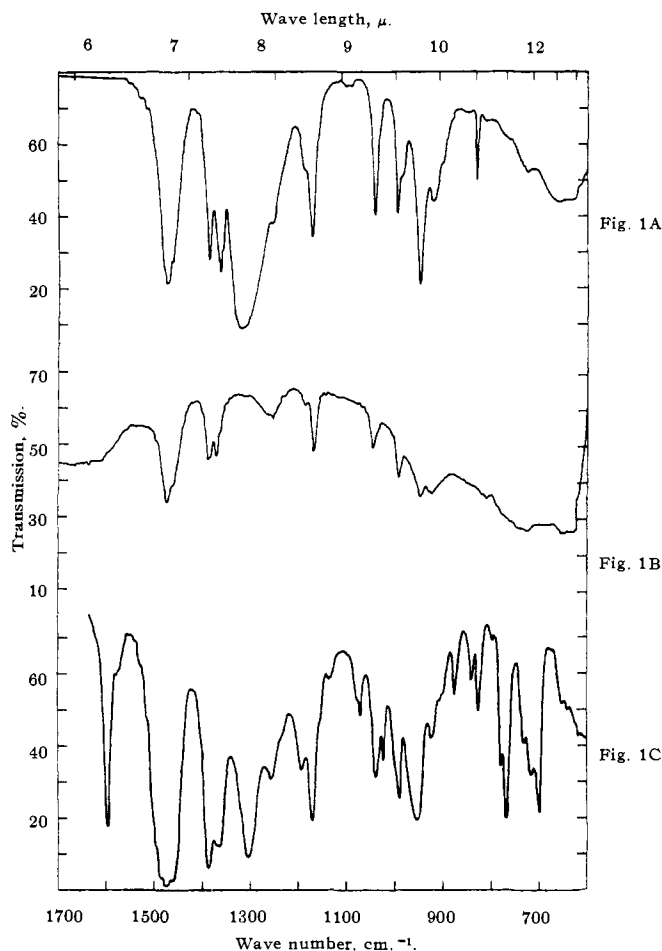
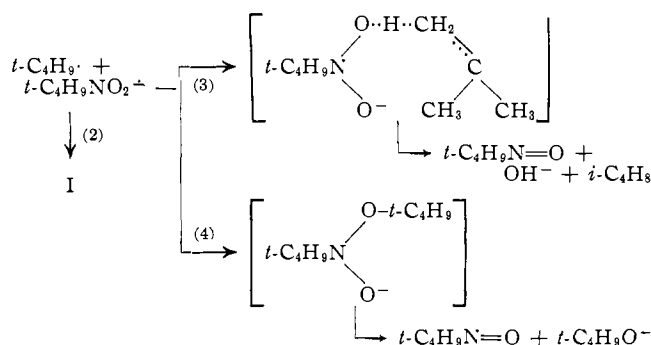


Fig. 1.—Infrared curves of unhydrolyzed solid products (Nujol mulls): 1A, solid from reaction of *t*-nitrobutane with sodium in glyme; 1B, solid from reaction of *t*-nitrobutane with sodium in glyme after removing sodium nitrite by trituration with 30% aqueous sodium hydroxide; 1C, solid from reaction of phenylsodium with *t*-nitrobutane in toluene.

enges *t*-butyl radicals faster than it decomposes. It is apparent therefore, that eq. 2–4 constitute the initial steps in major product formation.



Process 2 is analogous to a radical dimerization resulting in bond formation between atoms supporting the highest odd electron density. Thus, C–N bond formation might be anticipated since the odd electron in nitro anion radicals is considered to be largely localized on the nitrogen atom.<sup>9a,b</sup> An alternative

(4) B. Oddo, *Atti reale Accad. Lincei Roma* [5] **13**, II, 220 (1904); *Chem. Zentr.*, **75**, II, 1113 (1904).

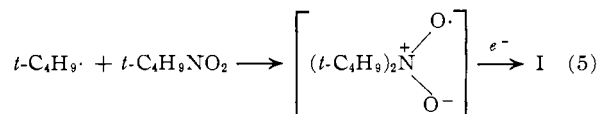
(5) H. Hepworth, *J. Chem. Soc.*, **117**, 1004 (1920).

(6) G. D. Buckley, *ibid.*, 1492 (1947).

(7) R. H. Pickard and J. Kenyon, *Proc. Chem. Soc.*, **23**, 153 (1907).

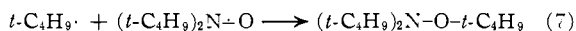
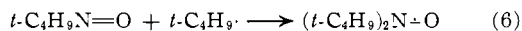
(8) A. K. Hoffmann, A. M. Feldman, and E. Gelblum, *J. Am. Chem. Soc.*, **86**, 646 (1964).

(9) (a) J. C. Schug, T. H. Brown, and M. Karplus, *J. Chem. Phys.*, **37**, 330 (1962). (b) The hyperfine coupling constants (h.c.c.'s) of the nitrogen atom in nitro anion radicals serve as an index of the unpaired electron density at nitrogen. The greater h.c.c. of aliphatic nitro anion radicals as opposed to their aromatic homologs (D. H. Geske and J. L. Ragle, *J. Am. Chem. Soc.*, **83**, 3532 (1961)) indicates that such unpaired electron density on the nitrogen atom in the former is more pronounced.



route to I (5) is rejected because under identical reaction conditions 2-nitro-2,4,4-trimethylpentane (*t*-nitro-octane) formed only sodium nitrite and no solid analogous to I.<sup>3</sup> Although *t*-octyl radicals were formed in the presence of *t*-nitrooctane, substantially no reaction occurred between the radicals and the nitro compound. Similar behavior for 2-phenyl-2-propyl radicals in the presence of 2-nitro-2-phenylpropane has also been observed. The failure of these radicals to react significantly with their corresponding nitro compounds implies that they possess sufficient selectivity to discriminate between starting nitro compound and another radical. Such discrimination is not unexpected because during radical-radical reactions two relatively high energy species are dissipated while reaction with nitro compound results in a species still retaining radical character to which it is difficult to ascribe any special stabilization.

Like 2, 4 involves combination of the *t*-butyl radical with the *t*-nitrobutyl anion radical but at oxygen rather than nitrogen. The adduct so produced is identical with that which would arise from the addition of *t*-butoxide ion to *t*-nitrosobutane and may be expected to dissociate to these two products. As evidenced by the minor amount of *t*-butyl alcohol, attack of *t*-butyl radicals on oxygen occurs less frequently than on nitrogen. This is reasonable in view of the high electron density at the nitrogen atom. Hydrogen transfer (3), suggested by primary product isobutylene (Table I), finds similarity to those occurring between hydrocarbon radicals and radicals in which the odd electron is localized at a hetero atom.<sup>10</sup> *t*-Nitrosobutane, however, common to both 3 and 4, could not be detected. This is not surprising in view of the known reactivity of nitroso compounds toward free radicals, evidenced by their ability to inhibit polymerization<sup>11</sup> and their reaction with radicals to form the corresponding tri-substituted hydroxylamines.<sup>12,13a,b</sup> This reactivity, coupled with the information that *t*-nitrobutane anion radical formed throughout the course of reduction is a continuous source of *t*-butyl radicals, leads to the presumption that *t*-nitrosobutane is the precursor of tri-*t*-butylhydroxylamine *via* intermediate di-*t*-butylnitroxide (6 and 7).



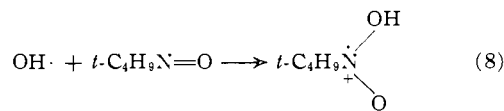
The formation of di-*t*-butylnitroxide by the addition of *t*-butyl radicals at room temperature to *t*-nitrosobutane (6) has been independently confirmed.<sup>14</sup> Like *t*-nitrosobutane, di-*t*-butylnitroxide is also a vigorous free radical scavenger. Subsequent work<sup>15</sup> has shown it to be an effective antioxidant, polymerization inhibitor, and radical trap. It should, therefore, exist in the presence of *t*-butyl radicals in only low steady state concentrations because of preferential conversion (7) to tri-*t*-butylhydroxylamine. This interpretation is fully consistent with the low concentrations of di-*t*-

butylnitroxide observed in solution as shown in Table I.<sup>16</sup>

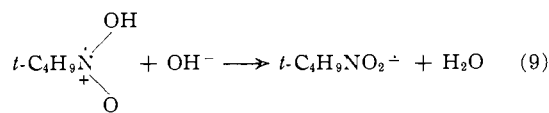
Further support for 6 and 7 is provided by the results of reducing *t*-nitrobutane in the presence of tritiated *t*-nitrosobutane. Tri-*t*-butylhydroxylamine isolated from this reaction contained 7.8% of the starting activity, but the solid (retaining its ability to form di-*t*-butylnitroxide on hydrolysis) contained none. *t*-Nitrosobutane, therefore, while not a precursor of I, is undoubtedly an intermediate in the formation of tri-*t*-butylhydroxylamine and also of di-*t*-butylnitroxide which is observed in solution.

In addition to the products so far discussed, minor amounts of others are formed as shown in Tables I and III. Although the mechanisms by which they are formed are more elusive, possible routes for some may be suggested. Thus, N,N-di-*t*-butylhydroxylamine may be formed by sodium reduction of di-*t*-butylnitroxide. Indeed, this has been independently observed. N,O-Di-*t*-butylhydroxylamine may arise *via* the attack of a *t*-butyl radical on the oxygen atom of *t*-nitrosobutane followed by either hydrogen atom transfer or reduction of the resulting hydroxylamino radical. *t*-Butylamine and N-*t*-butylhydroxylamine may both arise *via* sodium reduction of *t*-nitrosobutane. Further speculation is unwarranted in view of the small amounts of these products.

The proposed route to tri-*t*-butylhydroxylamine together with small amounts of di-*t*-butylnitroxide in solution indicated that these products could be obtained if one were to generate the *t*-nitrobutyl anion radical in the presence of *t*-nitrosobutane by some alternate means. The possibility of achieving an alternate route<sup>17</sup> to the *t*-nitrobutyl anion radical stemmed from the hope that hydroxyl radicals would add to *t*-nitrosobutane to form the conjugate acid of the *t*-nitrobutyl anion radical (8). The relatively long lifetime of the



*t*-nitrobutyl anion radical suggested that its conjugate acid might survive sufficiently long to be neutralized by base (9). Anion radical so formed would undergo



scission to a *t*-butyl radical which could react *via* 6 and 7. In agreement with anticipation, it was found that the addition of sodium peroxide to aqueous glyme solutions containing ferrous sulfate resulted in the formation of di-*t*-butylnitroxide in amounts detectable by e.s.r. Tri-*t*-butylhydroxylamine, however, could not be detected by v.p.c.

**Reactions of Solid.**—In view of structure I assigned to the organic portion of the solid, it is instructive to consider its thermal and hydrolytic decomposition. The routes by which these reactions proceed are unknown in detail. Several paths, however, are suggested by the structure of I and are satisfying in that they are self-consistent. As seen from Tables I and IV, tri-*t*-butylhydroxylamine is a product common to both reduction of *t*-nitrobutane with sodium and the thermal decomposition of the solid. Because di-*t*-butylnitroxide is an avid radical scavenger, the formation of tri-*t*-butylhydroxylamine is taken as diagnostic

(16) The small amounts of nitroxide found in the reaction of sodium with other nitro compounds<sup>3</sup> presumably arise by a similar mechanism.

(17) This reaction was suggested by Dr. E. F. Ullman of these laboratories.

(10) K. O. Kutschke and E. W. R. Steacie, "Vistas in Free-radical Chemistry," Supplement No. 3 to *Tetrahedron*, Pergamon Press, New York, N. Y., 1959, p. 183 ff.

(11) S. J. Foord, *J. Chem. Soc.*, 48 (1940).

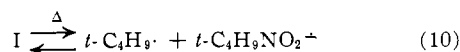
(12) B. A. Gingras and W. A. Waters, *ibid.*, 1920 (1954).

(13) (a) L. Phillips, *Proc. Chem. Soc.*, 204 (1961); (b) A. Maschke, B. S. Shapiro, and F. W. Lampe, *J. Am. Chem. Soc.*, **85**, 1878 (1963).

(14) J. G. Calvert, Ohio State University, private communication.

(15) Work by A. K. Hoffmann, A. M. Feldman, and E. Gelblum to be published.

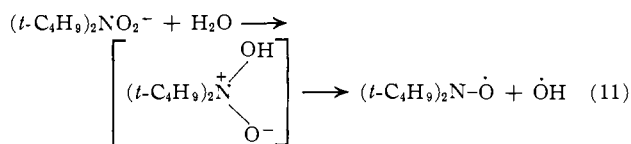
of the formation of *t*-butyl radicals. It is indicated therefore, that the solid is a source of *t*-butyl radicals under these conditions.<sup>18</sup> In addition, *t*-nitrobutyl anion radicals are suggested to be present by the lavender color suffusing the solid during decomposition. This color is identical with that observed in solution during the reduction of *t*-nitrobutane by sodium. A reversal of 2 symbolized by 10 is proposed to account for both these spe-



cies. Equilibrium is driven to the right by the instability of *t*-nitrobutyl anion radical and by competing reactions such as those proposed to occur in solution. Reactions 1-4 and 6-7 account for the majority of the products in Table IV. The remaining products can also be rationalized by processes involving *t*-butyl radicals. Thus, *t*-butyl radicals may, to a small extent, transfer a hydrogen atom to di-*t*-butylnitroxide forming the N,N-di-*t*-butylhydroxylamine while hydrogen atom transfer from nitroxide to *t*-butyl radicals or disproportionation between *t*-butyl radicals might be responsible for the formation of isobutane.

In contrast to its behavior during thermal decomposition, the solid reacted hydrolytically to form substantial amounts of di-*t*-butylnitroxide while no tri-*t*-butylhydroxylamine was detectable. The absence of tri-*t*-butylhydroxylamine indicates that *t*-butyl radicals are *not* generated from the solid during hydrolysis and that di-*t*-butylnitroxide is *not* formed under these conditions by the attack of a *t*-butyl radical on *t*-nitrosobutane as in 6. This conclusion is strongly supported by failure to intercept *t*-butyl radicals during the hydrolysis of solid. Thus, if 6 were operational under hydrolytic conditions, *p*-nitrosodimethylaniline should compete against *t*-nitrosobutane as a radical trap. Hydrolysis under these conditions, however (Table II), led not to a decreased, but rather to a slightly increased, yield of di-*t*-butylnitroxide.

The ability of I to withstand exposure to a strongly alkaline aqueous solution indicates that protons are required for its hydrolysis. Protonation of I gives an intermediate which is suggested (11) to decompose to



nitroxide and a hydroxyl radical. The latter has been detected by the blue chemiluminescence<sup>19</sup> accompanying the hydrolysis of either I or II by aqueous luminol. The hydroxyl radicals do not dimerize to hydrogen peroxide since it could not be detected by starch-iodide. While their fate is unknown, they are probably dissipated by oxidation of both product nitroxide and solvent. As seen from Table II, more *t*-nitrosobutane and isobutylene are formed in heptane than in glyme. Furthermore the increase in *t*-nitrosobutane is roughly equivalent to the decrease in di-*t*-butylnitroxide. Since *t*-nitrosobutane and isobutylene result from the oxidation of di-*t*-butylnitroxide,<sup>15</sup> the difference between the yields of di-*t*-butylnitroxide in heptane and glyme is probably related to the relative reactivity of each solvent toward hydroxyl radicals.

(18) During this decomposition tri-*t*-butylhydroxylamine is not produced via the decomposition of di-*t*-butylnitroxide. Although di-*t*-butylnitroxide disproportionates at temperatures in excess of 125° to form *t*-nitrosobutane and tri-*t*-butylhydroxylamine<sup>16</sup> (which subsequently decomposes), it does not decompose over extended periods of time at 100°.

(19) W. Langenbeck and U. Ruge, *Ber.*, **70**, 367 (1937).

## Conclusion

It has been shown that di-*t*-butylnitroxide is formed by the hydrolysis of a solid having properties consistent with its formulation as sodium di-*t*-butylhydroxylamine oxide. This material is considered to arise by a combination of the *t*-butyl radical with *t*-nitrobutyl anion radical and its structure is strongly supported by an independent synthesis of an analogous compound. This latter reaction, involving the direct addition of an anion to a nitro compound, makes available a variety of nitroxides and is discussed in the following publication.

## Experimental<sup>20</sup>

**Materials.**—1,2-Dimethoxyethane (glyme, Ansul Chemical Co.) was predried for several days over calcium hydride, filtered, and distilled from lithium aluminum hydride at atmospheric pressure under nitrogen directly into the reaction flask immediately prior to use. *t*-Nitrobutane was prepared from *t*-butylamine (Distillation Products Ind.) by the procedure of Kornblum.<sup>21</sup> Sodium was weighed and cut into pieces 1 cm. on a side under cyclohexane directly before use. Prepurified nitrogen was used, and occasionally tanks were rejected because of excess moisture content as shown by reaction with benzophenone ketyl. With these tanks excepted, reactions run under ketyl-purified nitrogen and prepurified nitrogen used without further treatment showed no discernible differences.

**Instruments.**—All e.s.r. measurements were made on a Varian V-4500 electron spin resonance spectrometer with modulation frequencies of 400 c.p.s. or 100 kc.p.s.; n.m.r. spectra were recorded on a Varian V-4300 B n.m.r. spectrometer operating at 56.4 Mc. while the relative peak intensities were determined on a Varian V-3521 integrator. Tetramethylsilane was used as an internal standard and all chemical shifts are expressed on the  $\tau$ -scale.<sup>22</sup> Infrared spectra were recorded on a Beckman spectrophotometer, Model IR-4.

**Gas Chromatographic Analyses.**—The internal standard method of analysis was used. Analyses were run using known compounds as standards *vs.* ethylbenzene as the internal standard. Weight ratio *vs.* area ratio was plotted for the standard *vs.* ethylbenzene for each compound determined. These plots were linear. Duplicate v.p.c. runs were reproducible within 2% for each component of the same sample.

Two columns, both maintained at 110°, were used. The first was a 6-ft., 0.25-in. o.d. column packed with diisodecyl phthalate supported on 60-80 mesh Chromosorb W and was used to analyze for isobutylene, *t*-nitrosobutane, *t*-butyl alcohol, *t*-butyl nitrate, and *t*-nitrobutane. The He flow rate was 20.7 ml./min. and the retention times relative to ethylbenzene were: isobutylene, 0.05; *t*-nitrosobutane, 0.10; *t*-butyl alcohol, 0.13; *t*-butyl nitrate, 0.50; *t*-nitrobutane, 0.58. The second column, 6 ft., 0.25 in., o.d., used for di-*t*-butylnitroxide and tri-*t*-butylhydroxylamine, was packed with silicone grease supported on 60-80 mesh Chromosorb W. The He flow rate was 222 ml./min. and the retention times relative to ethylbenzene were: di-*t*-butylnitroxide, 1.9; tri-*t*-butylhydroxylamine, 5.9. The minimum detectability for the latter two compounds was 1 and 0.5% of the total sample (including solvent) by weight.

**Di-*t*-butylnitroxide.**—A 12-l., 3-necked Morton flask containing 9 l. of freshly distilled glyme was equipped with a nitrogen inlet, outlet, and high speed stirrer. The flask was charged with 670 g. (6.5 moles) of *t*-nitrobutane and 149 g. (6.5 g.-atoms) of sodium cut into pea-sized pieces. Throughout these operations air was rigorously excluded from the flask. The stirrer, which had a stainless steel propeller-type blade, was started and initially operated at a speed just sufficient to draw the sodium through the blade (1-2000 r.p.m.). The temperature of the reaction was maintained at 25-30° by controlling the rate of stirring and by an air blast directed against the walls of the flask. As the reaction progressed the rate of stirring was increased to ensure good mixing. All the sodium had reacted at the end of 24 hr. After completion of reaction, the bulk of the glyme was removed at room temperature *in vacuo*. Heat was supplied to the glyme slurry by a water bath maintained at 20-25°. After most of the solvent had been removed, a thick colorless slurry remained to which 2 l. of water was added at room temperature. Further work-up did not require the absence of air. The red-brown organic layer was separated and the clear alkaline aqueous layer extracted with several 300-ml. portions of pentane until the pentane extract was substantially colorless. The combined organic layer, precooled to 0°, was washed thoroughly with two 500-ml. portions of ice-cold 0.25 N HCl to remove hydroxyl-

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

(21) N. Kornblum, R. J. Clutter, and W. J. Jones, *J. Am. Chem. Soc.*, **78**, 4003 (1956).

(22) G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

amines. The nitroxide layer was immediately washed with 500 ml. of cold water followed by 500 ml. of cold 0.2 *N* aqueous sodium hydroxide. The nitroxide layer was set aside at this point while the combined cold aqueous acidic layers were extracted with pentane until colorless. This pentane extract was then used to extract the aqueous sodium hydroxide layer after which it was washed once with water and combined with the nitroxide layer. After drying over anhydrous Drierite or magnesium sulfate, the nitroxide was fractionally distilled through a Nester and Faust Semiworks spinning band column. After forecuts of pentane and glyme containing *t*-nitrosobutane had been removed, di-*t*-butylnitroxide, b.p. 60° (11 mm.), was collected in a yield of 166.5 g., 38.6%. Until collection of this fraction was complete, the pot temperature during distillation was not allowed to exceed 100°. The product obtained in this way was substantially pure as shown by v.p.c. and by the identity of its infrared spectrum to that of an analytical sample. The latter was collected from a 2-m. preparative v.p.c. column packed with silicone grease supported on Celite maintained at 118°. In several runs identical with this, it was noted that despite the acid extraction, small amounts of *N,N*-di-*t*-butylhydroxylamine crystallized in the cooler portions of the fractionating column head. In these cases, repetition of the acid extraction procedure removed the contaminant after which the repurified product was fractionally distilled; effective magnetic moment:  $1.72 \pm 0.03$  B.M. (theor. 1.73 B.M.). Spin assays by e.s.r. found  $5.9 \times 10^{23}$  free spins per mole. The *g*-value is 2.0065 and the line width 8.5 gauss. Di-*t*-butylnitroxide has an ultraviolet spectrum showing  $\lambda_{\text{max}}^{\text{hexane}}$  225 (shoulder), 238, 465  $\mu$ ;  $\log \epsilon$  3.30, 3.33, 0.95. Its dipole moment measured by a method previously described<sup>23</sup> is 3.08 D. As shown by its unchanging magnetic susceptibility, di-*t*-butylnitroxide is stable indefinitely at room temperature.

*Anal.* Calcd. for  $\text{C}_8\text{H}_{18}\text{NO}$ : C, 66.60; H, 12.58; N, 9.71; mol. wt., 144. Found: C, 66.77; H, 12.90; N, 9.74; mol. wt. (cryoscopic in benzene), 149.

A second fraction, 49.6 g., consisting of tri-*t*-butylhydroxylamine, b.p. 85° (11 mm.), was collected. The colorless pot residue, 20 g., also consisted of tri-*t*-butylhydroxylamine (total yield 69.6 g., 21%). A sample was collected for analysis and n.m.r. from the same 2-m. preparative v.p.c. column maintained at 118° as described above; n.m.r. in  $\text{CCl}_4$ : two single peaks corresponding to two types of *t*-butyl groups at  $\tau$  8.75 and 8.83 in a ratio of 2:1, respectively.

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{27}\text{NO}$ : C, 71.57; H, 13.52; N, 6.97; mol. wt., 201. Found: C, 71.52; H, 13.36; N, 7.58; mol. wt. (vapor pressure thermistor), 210.

**Work-up of the Aqueous Acid Extract.**—The aqueous acid extracts of the crude di-*t*-butylnitroxide were concentrated by solvent evaporation at room temperature *in vacuo* and finally dried by azeotropic distillation with benzene. On cooling the benzene solution, 30.9 g. of *t*-butylhydroxylammonium chlorides precipitated. Comparison of the infrared and n.m.r. spectra of this mixture with authentic samples established the presence of *N,N*-di-*t*-butyl-, *N,O*-di-*t*-butyl-, and *N*-*t*-butylhydroxylammonium chlorides. The major constituent, *N,N*-di-*t*-butylhydroxylammonium chloride, could be obtained pure after several recrystallizations from acetonitrile followed by one from ethanol; m.p. 184°,<sup>1</sup> reported<sup>24</sup> m.p. 158°. Free di-*t*-butylhydroxylamine was obtained from the hydrochloride in essentially quantitative yield by stirring it under nitrogen in the presence of pentane with 30% aqueous sodium hydroxide. Separation of the organic layer followed by evaporation of the pentane *in vacuo* at 0°, leaves colorless solid *N,N*-di-*t*-butylhydroxylamine.<sup>1</sup> After sublimation at 50° *in vacuo*, it has m.p. 65–66° (sealed tube). The free base must be stored under nitrogen since upon exposure to air the solid or its solutions in ether or pentane turn red within several hours with the formation of di-*t*-butylnitroxide.

Authentic *N*-*t*-butylhydroxylamine was prepared by the method of Emmons<sup>25</sup> and converted to its hydrochloride, m.p. 298–299°.

*Anal.* Calcd. for  $\text{C}_4\text{H}_{12}\text{NOCl}$ : C, 38.24; H, 9.86; Cl, 28.23. Found: C, 38.07; H, 9.78; Cl, 28.46.

Reaction of bromine with di-*t*-butylnitroxide yielded *N,O*-di-*t*-butylhydroxylammonium bromide,<sup>15</sup> which after conversion to its free base followed by neutralization with hydrogen chloride gave the chloride, m.p. 164–165° dec.

*Anal.* Calcd. for  $\text{C}_8\text{H}_{20}\text{NOCl}$ : C, 52.88; H, 11.09; N, 7.71; Cl, 19.51. Found: C, 52.81; H, 10.76; N, 7.75; Cl, 19.72.

By comparison with the infrared spectra of authentic samples, *N,N*-di-*t*-butyl- and *N*-*t*-butylhydroxylammonium chlorides are estimated to comprise 50 and 25% of the mixture, respectively, while *N,O*-di-*t*-butylhydroxylammonium chloride comprises the remainder. The yields of the free bases corresponding to these

percentages of the mixture are calculated to be 12.3 g., 2.6%; 5.5 g., 0.9%; and 6.5 g., 1.2%, respectively.

**Reaction of *t*-Nitrobutane with Sodium.**—The procedure for a typical run is described. Glyme, 600 ml., was distilled into a 1-l., 3-necked Morton flask which had been predried at 130° and allowed to cool under nitrogen. The flask was then connected to a high-speed stirrer and fitted with a nitrogen inlet and outlet. *t*-Nitrobutane (40 g., 0.39 mole), previously dried over magnesium sulfate, and 8.9 g. (0.39 g.-atom) of sodium were then added all at once. All operations were conducted under conditions which strictly excluded air or moisture and were carried out under nitrogen.

The mixture was stirred gently at first, maintaining the temperature of the reaction mixture at 25–30° with an air stream directed against the walls of the flask. Reaction started at once as evidenced by the golden color assumed by the sodium and the lavender-blue color of the solution presumed to be due to the *t*-nitrobutyl anion radical. Within 0.5 hr. the reaction mixture had become opaque due to the precipitation of solid. Reaction was complete after 16–18 hr. The reaction mixture was transferred to a fritted glass funnel (Kontes grade C) predried at 130°. The funnel was equipped with a nitrogen inlet and outlet and the reaction mixture which consisted of a colorless precipitate and colorless supernatant layer was filtered. The solid was washed with several 150-ml. portions of ether and dried at room temperature *in vacuo*. The weight of solid was 43.0 g., 87.9% by weight of the starting materials. The solid was transferred in a nitrogen filled drybox to vials which were stored under nitrogen at –78°. The filtrates from such runs were examined by v.p.c. to give the results listed in Table I. The components of the filtrate were identified by comparison of v.p.c. retention times with those of authentic samples. Each component, with the exception of *t*-butyl nitrate, prepared by the method of Baker,<sup>26</sup> was additionally characterized by trapping it from v.p.c. and establishing the identity of its infrared spectrum with that of an authentic sample. Isobutylene was also characterized by its mass spectrum. The v.p.c. peaks from the filtrate showed a shoulder on the isobutylene peak due to incompletely resolved isobutane. The amount of isobutane was found to comprise 10% of the total hydrocarbon fraction by comparison with synthetic mixtures of known composition. After analytical samples had been removed, the bulk of the glyme was distilled from the filtrate under nitrogen at a pot temperature of 90–100°. Introduction of anhydrous hydrogen chloride into the distillate precipitated 0.5 g., 1.1%, of *t*-butylamine hydrochloride, m.p. 289–290°, identified by its infrared spectrum which was identical with that of an authentic sample. *t*-Butylamine escaped detection by v.p.c. because it remained adsorbed on the columns used. Samples of filtrate contained, by e.s.r.,  $6 \times 10^{-8}$  mole of di-*t*-butylnitroxide.

In other runs, the reaction mixture was hydrolyzed directly without prior isolation of the solid. In these cases reactions with sodium were carried out in a 250-ml. heavy walled erlenmeyer flask in a manner described earlier.<sup>3</sup> They were hydrolyzed by the addition of 50 ml. of deaerated water to the reaction mixture at 0°. No gas was evolved during this process. Samples of the upper organic layer were analyzed by v.p.c. to give the results reported in Table III. Examination of the aqueous phase from such runs established the presence of sodium nitrite in amounts roughly equivalent to half the starting nitro groups and half the starting sodium. Thus, polarographic analysis for nitrite ion in the aqueous phase from a run employing 15 g. (146 mmoles) of *t*-nitrobutane and 1 g. equiv. of sodium found 71 mmoles of nitrite ion. In another run carried out identically as above but employing 25 g. (240 mmoles) of *t*-nitrobutane and 5.6 g. (0.24 g. atom) of sodium in 250 ml. of glyme, 124 mmoles of sodium nitrite was found in the aqueous phase after hydrolysis by 50 ml. of water.

**Solid Phase (General).**—The solid was moderately stable in the absence of moisture and could be stirred in glyme at room temperature for at least 1 week with no significant decomposition. It was insoluble in a variety of anhydrous solvents at room temperature: heptane, benzene, xylene, acetone, methyl ethyl ketone, ether, glyme, diglyme, tetrahydrofuran, and dimethylformamide. Dimethyl sulfoxide also did not dissolve it but extracted small amounts of sodium nitrite. In the presence of hydroxylic solvents, such as methanol, isopropyl alcohol, *t*-butyl alcohol, and acetic acid, it decomposed rapidly with the formation of di-*t*-butylnitroxide. It decomposed similarly in the presence of hexamethylphosphoramide. The solid hydrolyzed instantly on exposure to water with the separation of a red-brown organic layer which contained di-*t*-butylnitroxide and other products as shown in Table II. When samples of solid were hydrolyzed in the dark by  $2 \times 10^{-3}$  *M* aqueous solutions of luminol they did so with intense blue chemiluminescence and the formation of di-*t*-butylnitroxide. Hydrolyses in the absence of luminol, however, were not chemiluminescent. Microscopic examination showed that the ultimate particle size of the solid was roughly 2–4  $\mu$ . Comparison of its X-ray powder diffraction

(23) S. A. Giddings and R. J. Best, *J. Am. Chem. Soc.*, **83**, 2393 (1961).

(24) F. Klages and H. Sitz, *Ber.*, **92**, 2606 (1959).

(25) W. D. Emmons, *J. Am. Chem. Soc.*, **79**, 5739 (1957).

(26) J. W. Baker and D. M. Easty, *J. Chem. Soc.*, 1193 (1952).



patterns with standard patterns established that it contained 25–40% by weight of sodium nitrite admixed with crystalline organic material. The infrared spectrum, Fig. 1A, shows inorganic nitrite (830, 1315  $\text{cm}^{-1}$ ), *t*-butyl groups (1170, 1360, 1385  $\text{cm}^{-1}$ ), and a pattern of bands in the 900–1050  $\text{cm}^{-1}$  region attributed to N–O single bonds and *t*-butyl groups. Samples sealed into tubes under nitrogen showed an e.s.r. spectrum of low intensity. The spectrum had a broad central line with two sharp lines separated by 30 gauss. The outer lines correspond to di-*t*-butylnitroxide in the liquid state. The center line of the nitroxide triplet was obscured by the broader internal line. The over-all intensity of the spectrum ( $10^{16}$  free spins/g.) corresponds to bulk diamagnetism of the solid. Several e.s.r. sample tubes containing solid were examined at different temperatures. The tubes were charged with solid under nitrogen, evacuated, and sealed. Some of the tubes contained diglyme, previously dried by distillation from lithium aluminum hydride *in vacuo*. The tubes were placed in the e.s.r. cavity and spectra recorded while the temperature was increased over a period of 1–3 hr. In each case, no significant change in spectrum was observed until a temperature of approximately 100° was reached. At this temperature and above, the signal due to di-*t*-butylnitroxide grew in intensity, ultimately becoming a single line, and the solid was colored red.

**Extraction of Solid with Aqueous Sodium Hydroxide.**—Solid, 4.8236 g., was slurried with 200 ml. of chilled 30% aqueous sodium hydroxide in a funnel under nitrogen and filtered rapidly in an effort to minimize decomposition. The alkaline extract contained 1.50 g. of sodium nitrite, which is equivalent to 31.1% of the weight of the starting solid. Assays of the alkaline filtrates from two other experiments which employed 18.87 and 5.45 g. of solid, established the presence of 5.48 and 1.63 g. of sodium nitrite, respectively. These, in the same order, correspond to 29.0 and 29.9% by weight of sodium nitrite in the solid. The cream colored residue was dried at room temperature *in vacuo* for about 1 hr. Its infrared spectrum, Fig. 1B, showed it to be free of sodium nitrite. Drying was accompanied by considerable loss of di-*t*-butylnitroxide and other volatiles. This is reflected in the relatively low yields of hydrolysis products, Table V. These data are not presented for their quantitative aspect, but only to demonstrate that the tritreated solid retained its ability to form di-*t*-butylnitroxide on hydrolysis. The hydrolysate aqueous layer was evaporated to dryness *in vacuo*. The infrared spectrum of the residue revealed the absence of sodium nitrite bands.

TABLE V  
PRODUCTS OF THE HYDROLYSIS OF SOLID WASHED WITH 30%  
AQUEOUS SODIUM HYDROXIDE

| Product                   | <i>i</i> -C <sub>4</sub> H <sub>8</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> ) <sub>2</sub> N+O |
|---------------------------|---|--|--|--|
| mmoles per 10 g. of solid | 4.1                                     | 11.9                                       | 6.9  | 4.4  |
| Wt. %                     | 2.3                                     | 10.4                                       | 5.1  | 6.4  |

**Reaction of Solid with Water.**—The solid hydrolyzed instantly whether it was exposed to water in the presence of solvent or not. In a moist atmosphere it developed a red color within several seconds. After standing in the atmosphere for 12 hr., it had completely hydrolyzed, di-*t*-butylnitroxide had been lost by volatilization, and only sodium nitrite with a smaller quantity of sodium hydroxide remained. Typical procedures for the hydrolysis of the solid are described.

1. **In Heptane.**—A 100-ml., 3-necked round-bottomed flask, previously dried at 130° and cooled under nitrogen, was fitted with a nitrogen inlet, outlet, thermometer, Teflon-coated magnetic stirrer, and serum cap. The flask was charged with 50 ml. of heptane and 5.5255 g. of solid against a nitrogen flow. The suspension was cooled in an ice-acetone bath and stirred while adding 15 ml. of deaerated water *via* a hypodermic syringe. The water was added at a rate such that the temperature did not exceed –2 to –3°. The reaction mixture consisted of two clear layers: the upper layer, greenish in color; the lower, colorless. After stirring for 1 hr., samples of the organic layer were analyzed by v.p.c. giving the results shown in Table II, run 3. The layers were then separated and the aqueous layer was analyzed for sodium hydroxide and sodium nitrite. An identical run employing 4.6025 g. of solid gave the results shown in Table II, run 4.

2. **In Glyme.**—Typical hydrolyses differed in no essential respect from those in the presence of heptane. After withdrawal of samples of the organic layer for v.p.c. analysis, the layers were separated and the glyme layer was extracted with saturated aqueous sodium chloride solution. The aqueous salt extract was combined with the initial aqueous layer for sodium nitrite and hydroxide assay. The results of two such runs employing 5.3639 (run 1) and 5.5567 g. (run 2) are reported in Table II.

3. **In Glyme with *p*-Nitrosodimethylaniline.**<sup>27</sup>—The solid, 5.8944 g., was added to a solution of 5 g. (33 mmoles) of *p*-nitro-

sodimethylaniline in 50 ml. of glyme and the mixture was hydrolyzed with 8 ml. of water at 0°. The reaction mixture was stirred at 0° for 1.5 hr. A sample of the organic layer was withdrawn for v.p.c. analysis to give the results listed in Table II. The aqueous alkaline layer was dark green to black in color and no products other than a small amount of *p*-nitrosodimethylaniline could be obtained from it after neutralization.

**Thermal Decomposition of Solid.**—A vial containing 5.1793 g. of solid was placed in a nitrogen-filled drying pistol which was connected through two traps to a vacuum train. The first trap was cooled in a slush of Dry Ice-acetone and the second with liquid nitrogen. The sample was heated at 140° (0.25 mm.) for 23 hr. Soon after heating was commenced the solid became lavender colored, eventually turning colorless after about 1 hr. At the end of the decomposition, heptane was added to each trap under nitrogen. The solutions were warmed to 0° and analyzed by v.p.c. The results of this run are listed in Table IV. Although N,N-di-*t*-butylhydroxylamine was found to be among the products, some uncertainty concerning the accuracy of the amount reported exists due to its tendency to be adsorbed on v.p.c. columns used.

The nonvolatile residue, 2.9792 g., was decomposed with water in the presence of heptane as described above for the solid hydrolyses. Analysis of this heptane layer by v.p.c. disclosed the absence of any organic material other than solvent. Assay of the aqueous layer established the presence of 2.03 g. (29.4 mmoles) of sodium nitrite and 0.394 g. (9.8 mmoles) of sodium hydroxide. Mass spectrometric analysis of portions of the gas samples from the liquid nitrogen trap established them to be largely isobutylene, 78.2 mole %, with a smaller amount, 20.2 mole %, of isobutane together with traces of unknowns. Similar results were obtained for decompositions carried out at 100°.

**Reaction of Solid with Methyl Iodide and Benzyl Chloride.**—Solid, 5 g., was added under nitrogen to 10 ml. of methyl iodide and allowed to stand at room temperature for 4 days. During this time, the mixture slowly turned pink and finally red. Spectroscopic examination of the solution diluted with hexane revealed the characteristic absorption of di-*t*-butylnitroxide at 465  $\mu$ . Similar experiments employing benzyl chloride also revealed the 465  $\mu$  band and established the presence of di-*t*-butylnitroxide. Di-*t*-butylnitroxide, in turn, reacts further with these halides to give products which will be described elsewhere.<sup>16</sup>

**Reaction of Solid with Acetic Anhydride.**—A slurry of solid, 6.0 g., in 50 ml. of ether under nitrogen was treated with 8 ml. of acetic anhydride added dropwise to the reaction mixture at 0°. A vigorous reaction occurred during which nitric oxide was evolved. No attempt was made to collect the volatile products. After addition was complete the reaction mixture consisted of a red supernatant and a colorless solid consisting largely of sodium acetate. The solution was found by v.p.c. to contain isobutylene, 0.71 g. of di-*t*-butylnitroxide, and 0.78 g. of tri-*t*-butylhydroxylamine in addition to acetic acid and unreacted acetic anhydride.

**Oxidation of Solid with Iodine.**—In a 150-ml., 3-necked flask, fitted with a thermometer, nitrogen inlet, outlet, and dropping funnel was placed a Teflon-coated magnetic stirring bar. The flask was thoroughly swept with nitrogen and charged with 4.3 g. of solid and 50 ml. of glyme. A solution of 2.6 g. (10 mmoles) of iodine in 70 ml. of glyme was added dropwise to the stirred suspension. The reaction mixture under nitrogen was cooled to 0° throughout the addition of iodine. After stirring for 1 hr. at 0°, v.p.c. samples of solution were withdrawn and gave the results reported in Table VI. The solid formed as a result of this reaction contained substantial amounts of sodium iodide. Gaseous products produced in this reaction were not analyzed.

TABLE VI  
PRODUCTS FROM THE OXIDATION OF SOLID WITH IODINE

| Product  | mmoles per 10 g. of solid | Wt. % |
|--|---------------------------|-------|
| <i>i</i> -C <sub>4</sub> H <sub>8</sub>                      | 1.0                       | 0.6   |
| <i>t</i> -C <sub>4</sub> H <sub>9</sub> NO                   | 1.7                       | 1.5   |
| ( <i>t</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> N–O | 14.6                      | 21.0  |
| <i>t</i> -C <sub>4</sub> H <sub>9</sub> NO <sub>2</sub>      | <1                        | <1    |

**Reduction of *t*-Nitrobutane–Sodium Reaction Mixture with Aqueous Sodium Borohydride.**—To a typical reaction mixture derived from 15 g. (0.146 mole) of *t*-nitrobutane and 3.35 g. (0.146 g.-atom) of sodium in 150 ml. of glyme was added under nitrogen 7 g. (0.18 mole) of sodium borohydride in 30 ml. of water. The borohydride solution was added all at once *via* hypodermic syringe to the reaction mixture chilled in an ice bath. Reaction was moderately exothermic and within seconds after addition a colorless two-phase system had formed. The organic layer contained no di-*t*-butylnitroxide and was separated and poured into ether containing hydrogen chloride. These operations were conducted with the exclusion of air; otherwise the organic layer rapidly turned red with the formation of di-*t*-butyl-

(27) A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green and Co., London, 1948, p. 550.

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  $10^{16}$  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  $2 \times 10^{-3}$  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 Wiltzbach.<sup>30</sup> After removal of tritium by pumping the sample at  $-180^\circ$  and 0.001 mm. for 2 to 3 hr., the total activity was  $30.7 \times 10^8$  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  $11.4 \times 10^8$  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 | (–C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> -<br>mmoles per 10 g. of |  |  |   |      |
|---------|---|--|--|---|------|
|         | <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  |
| 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  $5.40 \times 10^8$  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  $2.41 \times 10^8$  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  $10^{-3}$  M in di-*t*-butylnitroxide by e.s.r. No tri-*t*-butylhydroxylamine could be detected by v.p.c.

**Acknowledgments.**—The authors gratefully acknowledge the help of Mr. E. S. Everett for much of the v.p.c. work, Dr. J. S. Deonarine and his group for microanalyses, Mr. N. Colthup for infrared analyses, and Dr. J. Lancaster for n.m.r. spectra and their interpretation.

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

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RECEIVED APRIL 20, 1963

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.

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