The competitive experiment described between *cis*-piperylene and *trans–trans*-hexadiene enables us to estimate the effect of nonterminal location of a double bond upon its reactivity in cycloaddition. We conclude that one double bond of *trans–trans*-hexadiene undergoes cycloaddition with 1,1-dichloro-2,2-difluoroethylene 0.046 times as fast as a double bond of butadiene. There is thus a very substantial deactivating effect arising from terminal substitution on a double bond even by a methyl group. If the initial step in 1,2-cycloaddition bears any resemblance to the chain-propagating reaction in free radical polymerization, then this effect is not unexpected, it being well known that only terminal olefins are highly active participants in this reaction.

From the results of part II we know that in *trans–cis*-2,4-hexadiene the rates of cycloaddition to the two double bonds are not equal, there being a slight but definite preference for addition to the *cis* double bond. The bracketed figures in Table II represent an attempt to place these reactivities on a semiquantitative basis. First, we assume that by changing one of the double bonds of *trans–trans*-hexadiene from *trans* to *cis* we are affecting the reactivity of the remaining *trans* double bond in the same ratio as in going from *trans*- to *cis*-piperylene. The relative reactivity assigned to the *trans* double bond of *trans–cis*-hexadiene is then $0.046 \times 2.3/1.65 = 0.064$. From the relative total amounts of addition to the two double bonds of *trans–cis*-hexadiene, we then find a relative reactivity of 0.087 for the *cis* double bond. The further assumption that the reactivity of the *cis* double bond is increased by a further factor of 2.3/1.65 gives us an estimated 0.12 for the reactivity of a double bond in *cis–cis*-2,4-hexadiene. This is close to the 0.11 determined for 1,2-cycloaddition to cyclopentadiene, but the significant comparison here

would be with the total rate of 1,2- and 1,4-addition (0.70), which should reflect the rate of formation of the biradical. This rate, without regard to the subsequent branching of the reaction path into 1,2- and 1,4-addition (see part I), may indicate the favoring influence of forced coplanarity compared to the freer rotation, or at least libration, in *cis–cis*-2,4-hexadiene. This requires a nonbiradical element in the Diels–Alder reaction to be responsible for the acceleration of four orders of magnitude relative to the position which cyclopentadiene would otherwise hold.

Finally, if we suppose that the reactivities of the nonterminal double bonds in the piperylenes are related to the corresponding reactivities in the hexadienes as the measured rates in the piperylenes themselves are to that of butadiene, we obtain the bracketed estimates of 0.053 and 0.028 for the relative rates of addition of 1,1-dichloro-2,2-difluoroethylene to the substituted double bonds of *cis*- and *trans*-piperylenes, respectively. This estimate calls for 2.3 and 1.7% of the unfavored product to be found in the cycloadduct. Such amounts if present should be detectable in the absence of special problems of resolution.

We conclude from this kinetic study that 1,2-cycloaddition of 1,1-dichloro-2,2-difluoroethylene and 1,4-cycloaddition of maleic anhydride are governed by entirely different factors. In the former reaction the effect of chlorine substitution in the 2-position and of methyl substitution in the 2- and 4-positions can be fully rationalized in terms of a reaction mechanism involving a biradical intermediate. The special effects due to polar character, blocking of *cisoid* diene conformation, and cyclic character of the diene, all of which are familiar in the Diels–Alder reaction, are absent here.

Cleavage Reactions of Tertiary Nitro Anion Radicals

BY A. KENTARO HOFFMANN, WILLIAM G. HODGSON, DONALD L. MARICLE, AND WALTER H. JURA

The chemical and electrochemical reductive behavior in glyme of the representative tertiary nitro compounds 2-nitro-2,4,4-trimethylpentane, 2-phenyl-2-nitropropane, 2,2-dinitropropane, and *t*-nitrobutane has been studied. Polarographic, cyclic voltammetric, and e.s.r. data are used to clarify the gross mechanistic features of the reactions of each nitro compound upon reduction by metallic sodium in glyme. For each compound, reduction leads to an intrinsically unstable anion radical which cleaves to nitrite ion and a corresponding free radical. The subsequent reactions of these free radicals, however, differ among the several nitro compounds. These reaction differences are related to whether the radical can be further reduced to anion under the reaction conditions and also to the lifetime of the parent nitro anion radical.

Introduction

While numerous stable anion radicals are known,[1–4] the existence of anion radicals which are unstable with respect to their decomposition into anions and radicals has only been postulated. Thus, electroreduction of alkyl halides[5] and the reductive dearylation of aryl phosphates[6] and triphenylphosphine oxide[7a,b] are presumed to proceed *via* cleavage of initially formed

anion radicals into anions and radicals. In an earlier communication[8] we have established that an unstable anion radical results from the reduction of *t*-nitrobutane. This decomposed to form a remarkably stable liquid free radical, di-*t*-butylnitroxide.[9] Subsequent work designed to elucidate the mechanism and scope of this unusual transformation has established that the reductive conversion of nitro compounds to their corresponding nitroxides in substantial yields is not general. The formation of nitroxide in substantial yields is, in fact, specific to *t*-nitrobutane among various nitro compounds studied. For other tertiary nitro compounds, reactions which do not form nitroxides predominate. It is the purpose of this paper to examine the reactions of anion radicals derived from

(1) D. E. Paul, D. Lipkin, and S. 1. Weissman, *J. Am. Chem. Soc.*, **78**, 116 (1956).

(2) T. R. Tuttle and S. I. Weissman, *ibid.*, **80**, 5342 (1958).

(3) A. Carrington and J. d. Santos-Veiga, *Mol. Phys.*, **5**, 21 (1962).

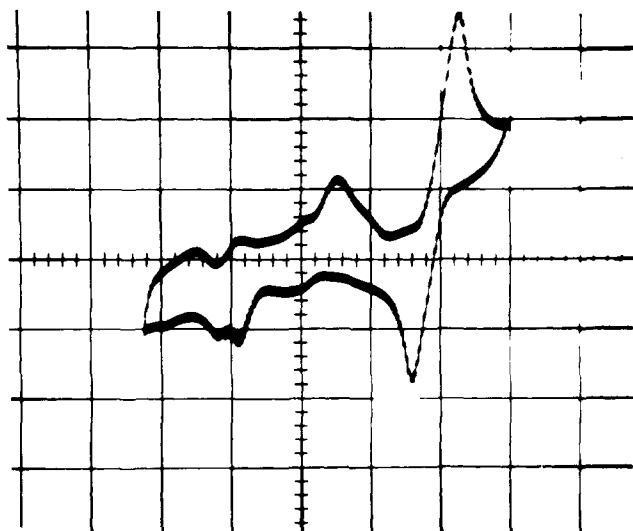(4) N. Hirota and S. I. Weissman, *J. Am. Chem. Soc.*, **82**, 4424 (1960).

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

(6) D. Lipkin, E. E. Jones, and F. Galiano, Preprints, Division of Petroleum Chemistry, 136th National Meeting of the American Chemical Society, Atlantic City, N. J., September 13–18, 1959, p. 11B.

(7) (a) A. K. Hoffmann and A. G. Tesch, *J. Am. Chem. Soc.*, **81**, 5519 (1959); (b) the results of subsequent work support the proposed mechanism and will be presented in a paper in preparation.

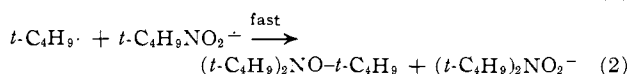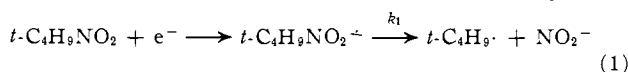(8) A. K. Hoffmann, W. G. Hodgson, and W. H. Jura, *J. Am. Chem. Soc.*, **83**, 4675 (1961).

(9) A. K. Hoffmann and A. T. Henderson, *ibid.*, **83**, 4671 (1961).
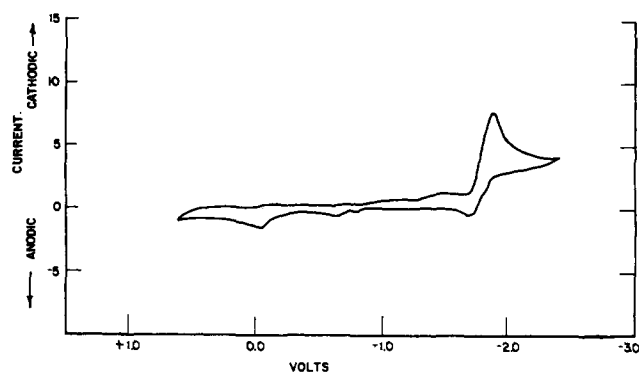
Fig. 1.—Cyclic voltammogram of t-nitrobutane at 0.12 v./sec.

Fig. 2a.—Cyclic voltammogram of t-nitrobutane at 1.2 v./sec.

Fig. 2b.—Cyclic voltammogram of t-nitrooctane at 30 v./sec.

in Fig. 1. Its instability is shown by the growth of the anion radical oxidation peak when the scan rate is increased by a factor of 10; Fig. 2a. In addition to the t-nitrobutyl anion radical peak there is also a peak at 0.0 v. corresponding to the oxidation of nitrite

several t-nitro compounds and to determine the reasons for the unique behavior of t-nitrobutane.
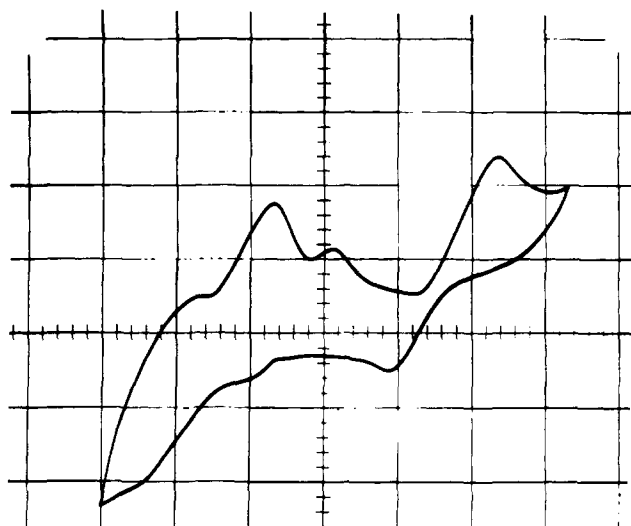
Results and Discussion

t-**Nitrobutane. Sodium Reduction.**—t-Nitrobutane is reduced in 1,2-dimethoxyethane (glyme) by metallic sodium to form the t-nitrobutyl anion radical which has been observed above the metal surface by e.s.r. The predominant products as seen from Table I are tri-t-butylhydroxylamine and an insoluble mixture of sodium nitrite with a salt formulated as sodium N,N-di-t-butylhydroxylamine oxide. The major reactions occurring during the reduction of t-nitrobutane may be summarized by 1 and 2. In addition, di-t-butylnitrox-

$$t\text{-}C_4H_9NO_2 + e^- \longrightarrow t\text{-}C_4H_9NO_2^{\cdot-} \xrightarrow{k_1} t\text{-}C_4H_9\cdot + NO_2^-$$

$$(1)$$

$$t\text{-}C_4H_9\cdot + t\text{-}C_4H_9NO_2^{\cdot-} \xrightarrow{\text{fast}}$$
$$(t\text{-}C_4H_9)_2NO\text{-}t\text{-}C_4H_9 + (t\text{-}C_4H_9)_2NO_2^- \quad (2)$$

ide together with other products are formed in solution in minor amounts. The hydroxylamine oxide salt forms di-t-butylnitroxide upon hydrolysis and finds no counterpart in the reduction products of the remaining nitro compounds. Its formation, proof of structure, and subsequent reactions are considered elsewhere.[10]

Electrochemical Reduction.—The formation of the t-nitrobutyl anion radical is clearly indicated by the clean one-electron polarographic reduction of t-nitrobutane as shown in Table II. The anion radical has been directly observed by cyclic voltammetry as shown

(10) A. K. Hoffmann, A. M. Feldman, E. Gelblum, and W. G. Hodgson, J. Am. Chem. Soc., **86**, 639 (1964).

TABLE I
PRODUCTS OF THE REDUCTION OF NITRO COMPOUND BY ONE EQUIVALENT OF SODIUM

Reactant	Products[a]	Yield, %
t-Nitrobutane	$(t\text{-}C_4H_9)_2NO_2^-Na^+$	83[b]
	$NaNO_2$	96–102
	$(t\text{-}C_4H_9)_2NO\text{-}t\text{-}C_4H_9$	21[c]
t-Nitrooctane	$(CH_3)_3CCH_2C\overset{CH_2}{\underset{CH_3}{\diagdown}}$	37,[d] 30[r]
	$(CH_3)_3CCH_2CH(CH_3)_2$	30,[d] 28[e]
	$\left((CH_3)_3CCH_2\overset{CH_3}{\underset{CH_3}{\diagdown}}C\right)$	18,[d] 17[e]
	$NaNO_2$	87,[d] 88[e]
t-Nitrocumene	$C_6H_5\overset{CH_3\ \ CH_3}{\underset{CH_3\ \ CH_3}{-C---C-}}C_6H_5$	61
	$C_{18}H_{22}{}^f$	5
	Biphenyl	8
	$NaNO_2$	90
2,2-Dinitropropane	$(CH_3)_2\overset{NO_2\ \ NO_2}{C---C}(CH_3)_2$	13
	$NaNC_2$	63

[a] Traces of nitroxide are present in each case in 10^{-3}–10^{-5} M amounts. The routes by which they are formed will be considered elsewhere.[10] [b] Yield was determined by difference and is based on the stoichiometry indicated by 1 and 2. [c] Yield based on four anion radicals forming one tri-t-butylhydroxylamine.[10] [d] Reaction run in diethyl ether. [e] Reaction run in glyme. [f] Unidentified isomer of bicumyl.

ion. It is estimated, from the scan rate required to just observe anion radical oxidation, that the lifetime of the t-nitrobutyl anion radical is of the order 0.1–1 sec. at room temperature. These results confirm the observation of the t-nitrobutyl anion radical by e.s.r. techniques. At the outset of electrolysis of a t-nitrobutane solution in glyme in the cavity of an e.s.r. spectrometer, a 3-line spectrum with a hyperfine coupling constant (h.c.c.) of 26.2 gauss was observed,
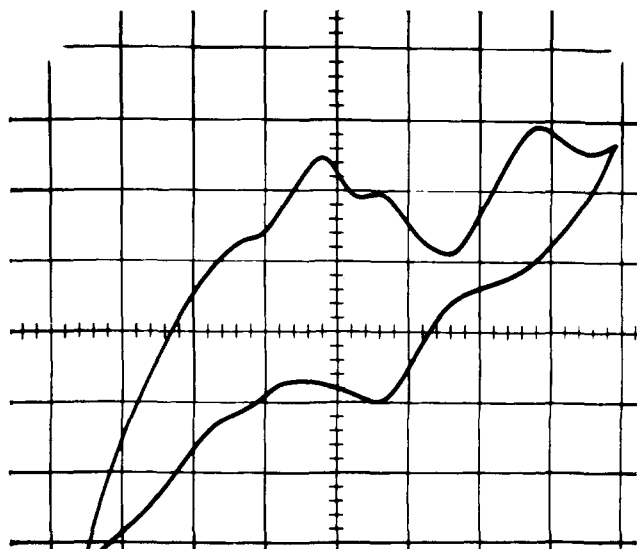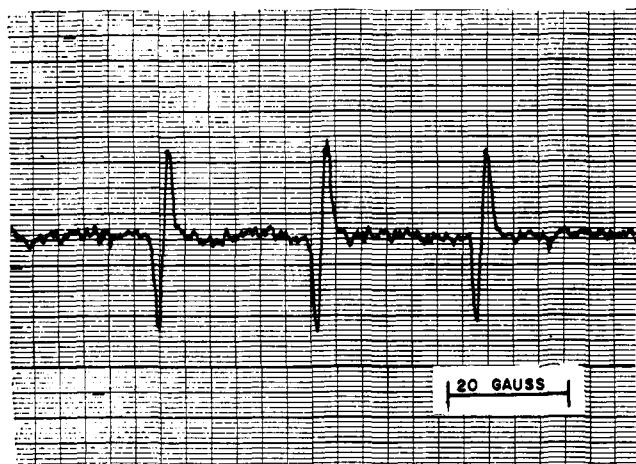
Fig. 2c.—Cyclic voltammogram of *t*-nitrooctane at 60 v./sec.

Fig. 3.—Anion radical of *t*-nitrobutane immediately following the start of *in situ* electroreduction of a glyme solution 2.7 m*M* in *t*-nitrobutane.

Fig. 3. The N^{14} h.c.c. is in excellent agreement with

TABLE II
POLAROGRAPHIC DATA

Compound	Concn., m*M*	$\epsilon_{1/2}{}^a$	I_d
t-Nitrobutane	0.444	−1.77	4.29[b]
2-Nitro-2,4,4-trimethyl-pentane	.247	−1.67	3.64
2-Phenyl-2-nitropropane	.439	−1.61	7.00
2,2-Dinitropropane	.687	−0.88 $(W_1)^d$	6.5 (W_1)
		−1.40 (W_2)	1.14 (W_2)
2,3-Dinitro-2,3-dimethyl-butane	.389	−1.38	7.17
Cumylpotassium	[e]	−1.6 to −1.7[c]	..
t-Butyl chloride	.946	No reduction	
t-Butyl bromide	.519	−2.39	7.54
t-Butyl iodide	.78	−1.59 (W_1)	3.94 (W_1)
		−2.49 (W_2)	3.79 (W_2)

 a These values were obtained with the three-electrode system. The $\epsilon_{1/2}$ values given must be considered as approximate. Because of the low dielectric constant of the solvent (7.0 at 25°), errors due to IR drop are not entirely eliminated with the 3-electrode system. Furthermore, $\epsilon_{1/2}$ values have not been corrected for the effect of following chemical reactions. *b* Background discharge occurs ∼0.1 v. early, indicating further reduction at very negative potentials; *i.e.*, −3.0 v. *vs.* s.c.e. *c* It is impossible to determine precisely the $\epsilon_{1/2}$ for the cumyl oxidation wave, owing to the presence of a maximum followed by a current minimum. *d* Because of the small current maximum the $\epsilon_{1/2}$ value for the first wave is approximate. *e* See Experimental section.
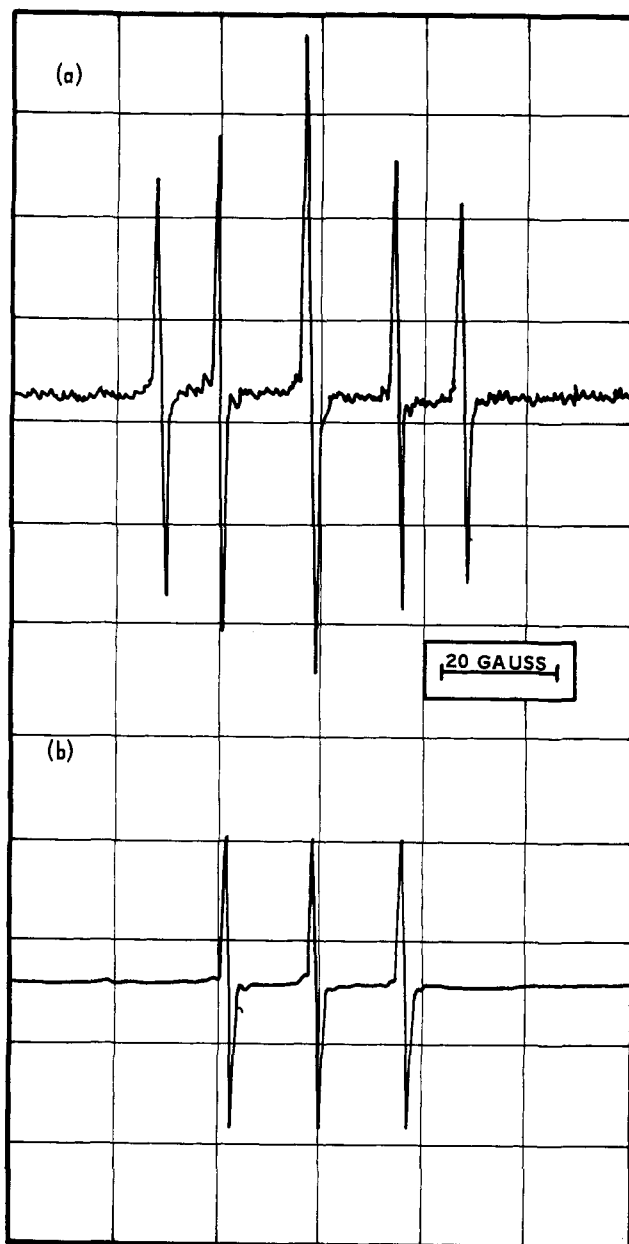

Fig. 4.—E.s.r. spectra of *in situ* electroreduction of *t*-nitrobutane 10 m*M* in glyme: (a) current on, *t*-nitrobutane anion radical and di-*t*-butylnitroxide; (b) current off, di-*t*-butylnitroxide. The gain was reduced by a factor of 5 between spectra a and b.

those of other aliphatic nitro anion radicals.[11a-c] On discontinuing the electrolysis, the spectrum of the nitro anion radical disappeared rapidly with the appearance of another 3-line spectrum with a h.c.c. of 15.4 gauss corresponding to di-*t*-butylnitroxide in glyme; Fig. 4b. The rate of disappearance of the *t*-nitrobutyl anion radical, measured by e.s.r., is strictly first order, with $k_1 = 1.05 \pm 0.05$ sec.$^{-1}$ corresponding to a half-life of 0.66 sec. at room temperature. This is in excellent agreement with the lifetime estimated by cyclic voltammetry. Continued electrolysis of such solutions results in the coexistence of the *t*-nitrobutyl anion radical and di-*t*-butylnitroxide, Fig. 4a, while current is being passed.

t-Butyl radicals have been indicated as initial products during the reduction of *t*-nitrobutane.[10] This, together with the electrochemical evidence so far

(11) (a) L. H. Piette, P. Ludwig, and R. N. Adams, *J. Am. Chem. Soc.*, **83**, 3909 (1961); (b) *ibid.*, **84**, 4212 (1962); (c) L. H. Piette, P. Ludwig, and R. N. Adams, *Anal. Chem.*, **34**, 916 (1962).
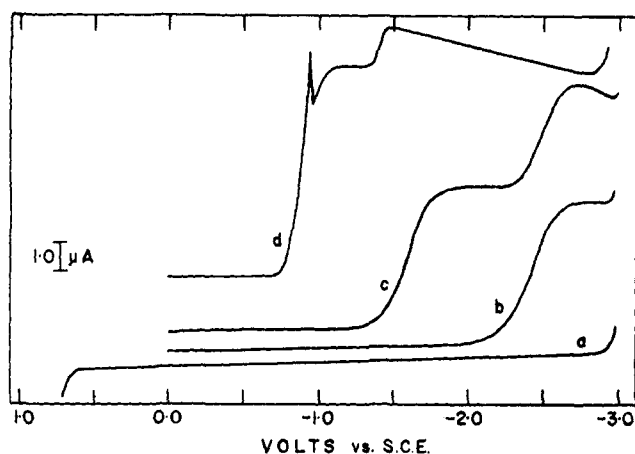
Fig. 5.—Polarograms of t-butyl halides and 2,2-dinitropropane in glyme: (a) glyme–0.1 M Bu$_4$NClO$_4$; (b) 0.45 mM t-butyl bromide; (c) 0.78 mM t-butyl iodide; (d) 0.69 mM 2,2-dinitropropane.

presented, clearly indicates the initial processes 1. With respect to subsequent processes symbolized by 2, however, it is necessary to consider whether further reduction of t-butyl radicals to anions may be significant. Evidence against the participation of anions is provided by the reduction potential of the t-butyl radical which was obtained by the polarographic reduction of the t-butyl halides in glyme. The generally accepted mechanism for the electroreduction of organic halides[5,12] is symbolized by 3, in which the first step is potential determining.

$$RX + e^- \longrightarrow RX^{-} \longrightarrow R\cdot + X^- \qquad (3)$$
$$R^- \xleftarrow{\;e^-\;} R–R$$
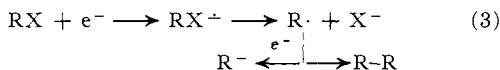
In terms of this mechanism two electrons are consumed in a single reduction step for t-butyl bromide (Table II, Fig. 5) because the first electron transfer requires a potential which is sufficiently negative to reduce the subsequently formed t-butyl radical to its anion. t-Butyl iodide, however, is reduced in two one-electron steps. The first electron is transferred at a potential that is 0.80 v. lower than that required by t-butyl bromide. Since, reasonably, 3 is operational for both t-butyl bromide and iodide, the second t-butyl iodide wave at -2.4 v. must correspond to the reduction of t-butyl radical to its anion.[12a]

This information strongly argues against the possibility of forming t-butyl anions in solution from the reduction of t-butyl radicals by t-nitrobutyl anion radicals (4). As seen from Table II, the difference in

$$RNO_2{}^{-} + R\cdot \rightleftarrows RNO_2 + R^- \qquad (4)$$
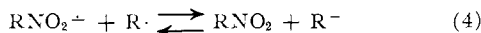
$\epsilon_{1/2}$'s for the reduction of t-nitrobutane and the reduction of t-butyl radical is 0.72 v. This difference in standard potentials corresponds to an equilibrium constant for 4 of 10^{-12}. Part of the observed potential difference, however, is due to the over-voltage for the irreversible second wave of t-butyl iodide and the instability of its reduction product.[13] The equilibrium

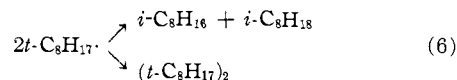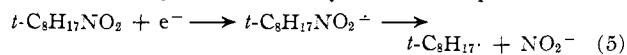(12) P. J. Elving and B. Pullman, Advan. Chem. Phys., 3, 1 (1961).

(12a) Note Added in Proof.—In opposition to a variety of alkyl iodides, benzyl and allyl iodides have recently been observed to reduce at a mercury electrode in two steps via organomercury intermediates (N. S. Hush and K. B. Oldham, J. Electroanal. Chem., 6, 34 (1963)). Undoubtedly, intermediates of this type are not involved in the reduction of t-butyl iodide in glyme. This halide reduces at a potential fully 1 v. more negative than that required by either benzyl or allyl iodide and lies in the potential region where numerous iodides which do not form organomercury intermediates become reduced.

(13) Most probably the major portion of the 0.72-v. difference in polarographic half-wave potential is due to the difference between the standard

constant for 4, therefore, must lie somewhat above 10^{-12} but still be substantially below unity.

In contrast to the electrolytic conditions, sodium metal probably has a sufficiently negative potential in glyme to effect reduction of t-butyl radicals to anions at its surface. Presuming a similar lifetime of the t-nitrobutyl anion radical at the sodium surface, diffusion from the surface results in the formation of t-butyl radicals in solution where they cannot be further reduced. This interpretation is reasonable in view of the relatively long lifetime of the t-nitrobutyl anion radical and its observation in solution above the reacting sodium surface. To the extent, however, that some t-butyl anions are formed at the sodium surface, the position of equilibrium 4 should result in a predominance of t-butyl radicals by electron exchange with starting nitro compound. This is only true, however, if equilibrium 4 is established prior to consumption of the t-butyl anion by competing reactions. The prior establishment of equilibrium 4 is indicated not only by the behavior of t-nitrocumene (vide infra), but also by the facility[14] and rapidity[15] of analogous exchanges. *Even at a sodium surface, therefore, the reactions of t-nitrobutyl anion radical probably occur predominantly via free radical intermediates.*

t-**Nitrooctane. Sodium Reduction.**—The principal products (Table I) of the reduction of t-nitrooctane by sodium clearly arise via t-octyl radicals, eq. 5 and 6.

$$t\text{-}C_8H_{17}NO_2 + e^- \longrightarrow t\text{-}C_8H_{17}NO_2{}^{-} \longrightarrow$$
$$t\text{-}C_8H_{17}\cdot + NO_2^- \quad (5)$$

$$2t\text{-}C_8H_{17}\cdot \begin{cases} i\text{-}C_8H_{16} + i\text{-}C_8H_{18} \\ (t\text{-}C_8H_{17})_2 \end{cases} \quad (6)$$

Their formation is evident from the high yield of sodium nitrite, the approximate equivalence of isooctene and isooctane, and the formation of the hitherto unknown dimer of the t-octyl radical, 2,2,4,4,5,5,7,7-octamethyloctane. Although it was anticipated that the steric requirements for t-octyl radical dimerization would favor disproportionation more exclusively, these results are in agreement with those of Evans[16] who found that during electrolysis of alkyl Grignard reagents the proportions of dimer obtained relative to solvent attack increased with increasing chain length of the Grignard. The reaction of t-nitrooctane with sodium, therefore, formally resembles a Wurtz reaction. It does not, however, suffer from the same mechanistic duality.[17] As reported elsewhere,[18] substantially no sodium nitrite results from the reaction of phenylsodium with t-nitrobutane. The nitro group, therefore, is neither eliminated nor displaced from a tertiary center by an energetic anion. This observation together with the marked unreactivity of tertiary carbon centers toward S$_N$2 displacements precludes the formation of dimer or disproportionation products by anionic displacement or elimination reactions.

Electrochemical Reduction.—Further support for 5 and 6 is given by the clean one-electron polarographic reduction of t-nitrooctane as shown in Table II. Cyclic voltammetry established that the t-nitrooctyl anion

potentials for the reactions

$$t\text{-}C_4H_9NO_2 + e^- \longrightarrow t\text{-}C_4H_9NO_2{}^{-}$$
$$t\text{-}C_4H_9\cdot + e^- \longrightarrow t\text{-}C_4H_9{}^-$$
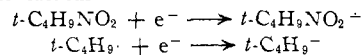
Although some uncertainty exists for the standard potentials, it is seen that even if they differ by only 0.5 v., the equilibrium constant for 4 is still $10^{-8.5}$.

(14) G. A. Russell and E. G. Janzen, J. Am. Chem. Soc., 84, 4153 (1962).

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

(16) W. V. Evans, D. Braithwaite, and E. Field, J. Am. Chem. Soc., 62, 534 (1940).

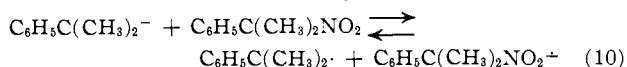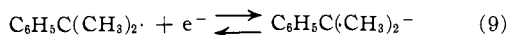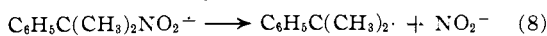(17) F. C. Whitmore and H. D. Zook, ibid., 64, 1783 (1942).

(18) A. K. Hoffmann, A. M. Feldman, and E. Gelblum, ibid., 86, 646 (1964).

radical is formed (Fig. 2b,c), but has a lifetime of several msec. or $1/_{250}$th that of the *t*-nitrobutyl anion radical. The failure to observe the *t*-nitrooctyl anion radical during electroreduction in the e.s.r. cavity is fully consistent with its short lifetime.
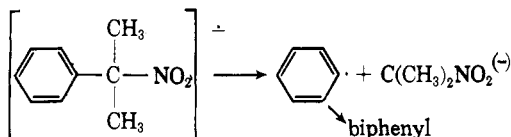
t-Nitrocumene. Sodium Reduction.—*t*-Nitrocumene is reduced by sodium to form largely bicumyl and sodium nitrite as shown in Table I. Product information alone suggests that the processes occurring during reduction are wholly analogous to those of *t*-nitrooctane.[19]

Electrochemical Reduction.—*t*-Nitrocumene undergoes a polarographic reduction in one wave corresponding to the uptake of two electrons as shown in Table II. This information requires that the lifetime of the *t*-nitrocumyl anion radical be very short and that the over-all reduction of *t*-nitrocumene proceed differently from that of *t*-nitrooctane. Thus, obtaining one-electron products *via* two-electron reduction results in an apparent dichotomy which is resolved by examining the polarographic behavior of the cumyl anion shown in Table II. Glyme solutions of *t*-cumylpotassium show an oxidation wave with an $\epsilon_{1/2}$ lying in the potential range -1.6 to -1.7 v. This, as seen from Table II, lies in the potential region of the upper portion of the *t*-nitrocumene reduction wave. In view of the similarity of potentials required for processes 7 and 9 it is possible for electron transfer from cumyl anion to *t*-nitrocumene to occur as in 10. It should be noted, how-

$$C_6H_5C(CH_3)_2NO_2 + e^- \rightleftarrows C_6H_5C(CH_3)_2NO_2{}^{\cdot-} \quad (7)$$

$$C_6H_5C(CH_3)_2NO_2{}^{\cdot-} \longrightarrow C_6H_5C(CH_3)_2\cdot + NO_2{}^- \quad (8)$$

$$C_6H_5C(CH_3)_2\cdot + e^- \rightleftarrows C_6H_5C(CH_3)_2{}^- \quad (9)$$

$$C_6H_5C(CH_3)_2{}^- + C_6H_5C(CH_3)_2NO_2 \rightleftarrows$$
$$C_6H_5C(CH_3)_2\cdot + C_6H_5C(CH_3)_2NO_2{}^{\cdot-} \quad (10)$$

$$2C_6H_5C(CH_3)_2\cdot \longrightarrow (C_6H_5C(CH_3)_2)_2 \quad (11)$$

ever, that under polarographic conditions cumyl anion reacts rapidly with the supporting electrolyte present. Under such conditions, therefore, 10 is improbable, thus leading to two-electron reduction. By contrast, 7–11 can occur during sodium reduction resulting in products arising from an over-all one-electron change. Because of the difficulty of relating $\epsilon_{1/2}$ to $\epsilon^{\circ 20}$ it is impossible to calculate an equilibrium constant for 10 precisely; however, a value in the range of unity or greater is consistent with the polarographic results. The over-all reaction 7–11 is rendered irreversible by the instability and subsequent reactions of both the *t*-nitrocumyl anion radical and the *t*-cumyl radical. Further support for the validity of 10 is afforded by the isolation of substantial quantities of bicumyl resulting from the reaction of cumylpotassium with *t*-nitrocumene in glyme.[21] Unlike *t*-nitrooctane, disproportionation products of the *t*-cumyl radical formed during sodium reduction of *t*-nitrocumene could not be detected either by v.p.c. or mass spectrometry, undoubtedly reflecting

(19) The route by which small amounts of biphenyl are produced remains unsettled. A reasonable path involves an alternate mode of collapse of the *t*-nitrocumyl anion radical similar to that observed for triphenylphosphine oxide[78] in which 2-nitropropyl anion is expelled followed by phenyl radical dimerization.

$$\left[\begin{array}{c} \text{CH}_3 \\ | \\ \langle\!\langle\text{—}\rangle\!\rangle\text{—C—NO}_2 \\ | \\ \text{CH}_3 \end{array} \right]^{\cdot-} \longrightarrow \langle\!\langle\text{—}\rangle\!\rangle\cdot + \text{C(CH}_3)_2\text{NO}_2{}^{(-)}$$
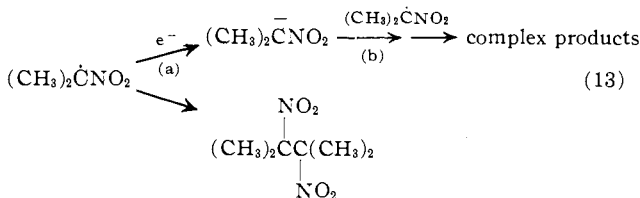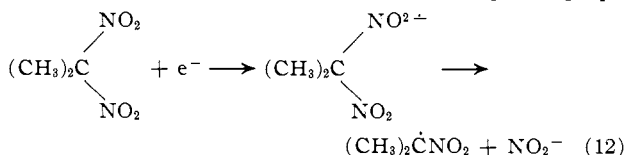$$\text{biphenyl}$$

(20) The standard potentials for 9 and the oxidation of the cumyl anion may differ slightly from the observed polarographic potentials by small over-voltages.

(21) The reaction of anions with nitro compounds which do not undergo electron exchange prior to reaction results in nitrogen containing products.[13]

the greater tendency of the *t*-cumyl radical to couple rather than disproportionate.[22]

In agreement with the above mechanism, the *t*-nitrocumyl anion radical is not observed by cyclic voltammetry, although nitrite ion is clearly evident. Although there is no direct evidence for the *t*-nitrocumyl anion radical at the electrode surface, analogy to *t*-nitrobutane and *t*-nitrooctane, together with the chemical evidence presented, suggest it as a logical intermediate. Its lifetime, however, must be quite short; less than 1 msec. *t*-Nitrocumene, while giving no observable anion radical on electrolysis in the e.s.r. cavity, formed only a very small concentration of a stable free radical with a triplet spectrum of three equally spaced equal intensity lines with an h.c.c. of 14.9 gauss. By analogy to *t*-nitrobutane, this species is assigned the structure bis-(2-phenyl-2-propyl)-nitroxide.[23]

2,2-Dinitropropane. Sodium Reduction.—The sodium reduction in glyme is complex. As shown in Table I, 13% of 2,3-dimethyl-2,3-dinitrobutane was isolated from the reaction mixture in addition to 63% sodium nitrite. The remaining material, a dark intractable tar, was not characterized. These results probably reflect subsequent reactions of the initial products. Thus, product molecules containing nitro groups may consume additional electrons becoming further reduced. They may also compete for radical intermediates since nitro compounds are recognized to react readily with free radicals.[24,25] The products are consistent with 12 and 13, support for which is found in the polarographic

$$(CH_3)_2C\!\!\begin{array}{c} {}^{NO_2}\!\!\nearrow \\ \searrow_{NO_2} \end{array} + e^- \longrightarrow (CH_3)_2C\!\!\begin{array}{c} {}^{NO_2{}^{\cdot-}}\!\!\nearrow \\ \searrow_{NO_2} \end{array} \longrightarrow$$
$$(CH_3)_2\dot{C}NO_2 + NO_2{}^- \quad (12)$$

$$(CH_3)_2\dot{C}NO_2 \xrightarrow[\;(a)\;]{e^-} (CH_3)_2\bar{C}NO_2 \xrightarrow[\;(b)\;]{(CH_3)_2\dot{C}NO_2} \longrightarrow \text{complex products}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (13)$$
$$\searrow$$
$$\begin{array}{c} NO_2 \\ | \\ (CH_3)_2\dot{C}C(CH_3)_2 \\ | \\ NO_2 \end{array}$$

reduction of 2,2-dinitropropane.

Electrochemical Reduction.—The sum of steps 12 and 13a has been inferred to constitute the initial step during the two-electron polarographic reduction of 2,2-dinitropropane in aqueous solution.[26] In glyme, however, as seen from Table II and Fig. 5, polarographic reduction of 2,2-dinitropropane occurs in two steps corresponding to 1.7 and 0.3 electrons, respectively. The first wave ($\epsilon_{1/2}$ -0.88 v.) is consistent with the reduction of *all* the material to an initial anion radical which subsequently cleaves; 70% of the resulting 2-nitropropyl radicals then undergo a one-electron reduction to 2-nitropropyl anions at this potential. The remaining 30% dimerize to 2,3-dimethyl-2,3-dinitrobutane which was shown independently to undergo the single two-electron reduction ($\epsilon_{1/2}$ -1.38 v.) corres-

(22) P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958).

(23) Additional evidence for this structural assignment arises from an alternate method of synthesis.[18]

(24) (a) R. A. Jackson and W. A. Waters, *J. Chem. Soc.*, 1653 (1960); (b) G. S. Hammond and P. D. Bartlett, *J. Polymer Sci.*, **6**, 617 (1951); (c) N. Inamoto and O. Simamura, *J. Org. Chem.*, **23**, 408 (1958).

(25) In this connection it is noteworthy that no products arising from the interaction of *t*-octyl or *t*-cumyl radicals with starting nitro compound have been isolated. This is probably due to the difference in activation energy for the reactions: R· + RNO₂ → products *vs.* R· + R· → products. The activation energy for the first reaction is probably higher than that of the second, since the activation energies of radical coupling reactions are known to be low. These considerations will be discussed further.[10]

(26) M. Masui and H. Sayo, *J. Chem. Soc.*, 4773 (1961)

ponding to the second wave of 2,2-dinitropropane. Like *t*-nitrocumene, no oxidizable nitro anion radical could be observed by cyclic voltammetry, but nitrite ion was visible. As expected for a short lived anion radical, none could be observed by e.s.r. during intracavity electrolysis.

Reactions of *t*-Nitro Anion Radicals.—The instability of the *t*-nitro aliphatic anion radicals to rupture of the C–N bond suggests that nitro anion radicals in general are intrinsically unstable. The anion radical of *t*-nitrobutane (and reasonably those of the remaining nitro compounds) undergoes a unimolecular collapse resulting in homolytic C–N bond fission to form a tertiary free radical and nitrite ion. A major portion of the driving force for this collapse probably is derived from the stability of the nitrite ion. This fission cannot occur for simple aromatic nitro anion radicals. These are stabilized by resonance with the ring; indeed, extensive delocalization of the odd electron over the conjugated π-system has been demonstrated.[27,28] Tertiary nitro anion radicals cannot be stabilized by resonance with their carbon moieties, however, and are therefore relatively less stable than their aromatic homologs.[29] In addition to lacking resonance with their carbon moieties, tertiary nitro anion radicals may also be less stable than their aromatic homologs by virtue of the greater stability of *t*-carbinyl radicals relative to aromatic radicals.[30]

Resonance effects, although influencing the lifetimes of the *t*-nitro anion radicals, cannot be solely responsible for the differences noted. Thus the observed differences in lifetimes between the *t*-nitrobutyl and *t*-nitrooctyl anion radicals cannot be accounted for on electronic grounds. These molecules differ, however, in the steric strains at their tertiary centers. All other factors being equal, a molecule more strained than another should show enhanced rates of reaction if the transition state affords strain relief. This effect has been noted in the 22-fold enhanced rate of solvolysis of *t*-octyl chloride relative to that of *t*-butyl chloride.[31] Since the homolytic fission of a C–N bond during the collapse of a nitro anion radical probably proceeds through a transition state where the groups about the tertiary carbon atom have a more nearly planar configuration than in the starting anion, it is anticipated that rate enhancements due to B-strain similar to or greater than those in chloride solvolyses will obtain. Furthermore, since a nitro group is larger than a chlorine atom, a more dramatic rate enhancement for the collapse of the *t*-nitrooctyl anion radical relative to the *t*-nitrobutyl anion radical is not unreasonable.[32]

In contrast to the *t*-nitrooctyl anion radical, the instability of the *t*-nitrocumyl and 2,2-dinitropropyl anion radicals relative to the *t*-nitrobutyl anion radi-
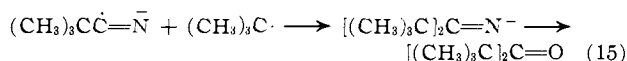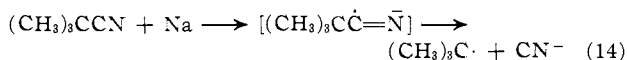
cal is more reasonably ascribed to electromeric effects. The free radicals generated by their collapse can be stabilized by resonance to which structures such as I and II contribute. The instability of the *t*-nitrocumyl

I   II
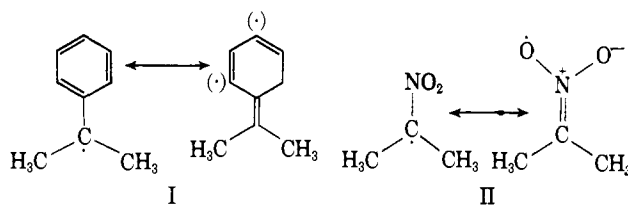
and 2,2-dinitropropyl anion radicals probably reflects a lowered activation energy for their collapse. This is undoubtedly due to the influence of the greater stability of I and II on the transition state, relative to the influence on the transition state of *t*-butyl or *t*-octyl radicals.

It was noted earlier that the synthetically significant di-*t*-butylnitroxide arising from the reduction of *t*-nitrobutane results from the hydrolysis of an initial product, sodium N,N-di-*t*-butylhydroxylamine oxide. The formation of this salt (1, 2) requires a bimolecular reaction between two reactive intermediates: *t*-butyl radical and *t*-nitrobutyl anion radical. Such a bimolecular reaction is reasonable in view of the relatively long lifetime and high steady-state concentration of the *t*-nitrobutyl anion radical as compared to the other nitro anion radicals. In contrast to *t*-nitrobutane, the products obtained from the remaining nitro compounds indicate that they are reduced to anion radicals which do not intercept other species to any appreciable extent. Rather than becoming directly involved in product-determining steps, they function predominantly as free radical sources. The failure of these nitro anion radicals to function effectively as scavengers for the free radicals they produce is undoubtedly due to their relatively short lifetimes, hence, low concentrations. The difference, therefore, between the reductive reactions of *t*-nitrobutane on one hand, and the remaining nitro compounds on the other, appears to reside almost wholly in the difference in lifetimes of their corresponding anion radicals.

The ideas developed in this paper may be generalized to other reactions. For example, the conversion of pivalonitrile by sodium to hexamethylacetone[33a,b] can easily be accounted for by 14 and 15.

$$(CH_3)_3CCN + Na \longrightarrow [(CH_3)_3C\dot{C}=\bar{N}] \longrightarrow$$
$$(CH_3)_3C\cdot + CN^- \quad (14)$$

$$(CH_3)_3C\dot{C}=\bar{N} + (CH_3)_3C\cdot \longrightarrow [(CH_3)_3C]_2C=N^- \longrightarrow$$
$$[(CH_3)_3C]_2C=O \quad (15)$$

Additionally, the formation and collapse of unstable anion radicals may provide an operational mechanism for the conversion of halides to organoalkali compounds by alkali metals and to Grignard reagents by magnesium.

Experimental[34]

t-Nitrobutane and 2-nitro-2,4,4-trimethylpentane were prepared by the method of Kornblum[35] and their purity established to be in excess of 95% by v.p.c. 2,2-Dinitropropane was used as purchased from K and K Laboratories, Inc.

2-Phenyl-2-nitropropane.—To 1 l. of anhydrous benzene under nitrogen containing 115 g. (1.02 moles) of nonalcoholic potassium *t*-butoxide was added 2-nitropropane (90 g., 1.01 mole) with stirring at room temperature. The temperature of the reaction mixture was maintained by gentle external cooling at 20-30° while

(27) R. L. Ward, *J. Chem. Phys.*, **30**, 852 (1959).

(28) R. L. Ward, *ibid.*, **32**, 410 (1960).

(29) It is noteworthy, in this connection, that several o-substituted aromatic nitro anion radicals have recently been reported whose h.c.c.'s approach those of aliphatic nitro anion radicals. This has been interpreted as arising from steric inhibition of nitro group resonance with the ring (D. H. Geske and J. R. Ragle, *J. Am. Chem. Soc.*, **83**, 3532 (1961)). Significantly, electrogeneration of the anion radicals of nitromesitylene and 1,3,5-tri-*t*-butylnitrobenzene has revealed (unpublished work by A. K. Hoffmann, A. M. Feldman, W. G. Hodgson, and W. H. Jura) that they are unstable, decomposing over a period of several minutes.

(30) C. S. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 50.

(31) H. C. Brown, *Record Chem. Progr.*, **14**, 83 (1953).

(32) An additional steric factor operating to increase the difference in stability between the *t*-nitrooctyl and *t*-nitrobutyl anion radicals may arise *via* solvation or ion pairing. For example, the effective size of the nitro group in the anion radical may be increased over that of the nitro compound by close association of either solvent or counter ion. The importance of both solvation (A. P. Krapcho and A. A. Bothner-By, *J. Am. Chem. Soc.*, **81**, 3658 (1959)) and ion pairing (S. I. Weissman and F. C. Adam, *ibid.*, **80**, 1518 (1958)) in anion radical chemistry is well recognized

(33) (a) V. L. Hansley (to E. I. du Pont de Nemours and Co.), U. S. Patent 2,742,503 (1956); (b) the authors are grateful to Dr. H. Hartzler for calling this reaction to their attention.

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

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

317 g. (1.0 mole) of diphenyliodonium chloride[36] was added slowly over the course of 4 hr. The reaction mixture was allowed to stir overnight prior to the addition of 2 l. of water. The organic layer was separated and the aqueous layer was extracted with two 200-ml. portions of benzene which were combined with the initial benzene layer. The solvent was removed by vacuum evaporation to leave a residue which was fractionally distilled in a Nester and Faust Semiworks spinning band column. After a forerun of iodobenzene, the fraction boiling at 105° (4 mm.) consisted of substantially pure 2-phenyl-2-nitropropane; yield 104.8 g., 63%. Although a pale yellow impurity was present in this material it could easily be removed by passing it over a short column of alumina to give product of analytical purity; n^{25}D 1.5205.

Anal. Calcd. for $C_9H_{11}O_2N$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.53; H, 7.00; N, 8.39.

General Procedure for Sodium Reactions.—Into a 250-ml. heavy-walled erlenmeyer flask were placed some ragged pieces of 5-mm. glass rod which served to abrade the alkali metal surface, and a Teflon-coated magnetic stirring bar. Directly before use, the flask and contents were predried for several hours at 130° and allowed to cool in a nitrogen atmosphere. A weighed amount of nitro compound was then added to the flask; glyme, previously refluxed over lithium aluminum hydride and stored in a reservoir over lithium aluminum hydride, was distilled under nitrogen directly into the reaction flask immediately prior to use. The flask was then fitted with an adapter having a nitrogen inlet, an exit *via* a mercury bubbler, and provision for the addition of reagents. A weighed amount of clean sodium metal cut into *ca.* 5-mm. pieces was added against a flow of nitrogen to the flask, the system was stoppered, the nitrogen flow stopped, and stirring begun. All reactions were conducted at 25-30°. Reactions conducted in this way started as soon as the sodium was added even prior to the commencement of stirring as evidenced by diffusion of color from the sodium surface into bulk solution or strong etching of the metal surface. Reactions which did not start immediately on addition of metal indicated scavenging of impurities by the system and were discarded. Stirring was continued until all metal had reacted, after which the reaction mixtures were worked up as described for each individual nitro compound. Details for the reaction of *t*-nitrobutane with sodium are described in the succeeding publication.[10]

Reaction of 2-Nitro-2,4,4-trimethylpentane (*t*-Nitrooctane) with Sodium in Glyme.—*t*-Nitrooctane (15.9 g., 100 mmoles) in 100 ml. of glyme was stirred with 2.3 g. (100 mg.-atoms) of metallic sodium. At the outset of reaction the sodium was brightly silver colored and the reaction was quite exothermic. In larger runs, external cooling was found necessary to prevent too rapid an exotherm. The sodium had completely reacted at the end of 24 hr., and the reaction mixture consisted of colorless solid with a pale yellow to colorless supernatant. The reaction mixture was filtered under nitrogen and the solid washed with several small portions of ether or heptane prior to drying *in vacuo*. It consisted wholly of sodium nitrite which was determined by assay to be 6.09 g. (88 mmoles). The glyme filtrate was analyzed by v.p.c prior to exposure to air or moisture and contained 3.19 g. (28 mmoles) of isooctane, 28%; 2,4,4-trimethylpentene-1, 3.39 g. (30 mmoles, 30%); and 0.487 g. (3 mmoles) of recovered 2-nitro-2,2,4-trimethylpentane. In pilot runs these constituents were isolated by preparative v.p.c. and characterized by the identity of their infrared spectra with those of authentic samples and by mass spectroscopy. In addition, 1.92 g. (8.5 mmoles, 17%) of a saturated hydrocarbon, $C_{16}H_{34}$, was present, identified by n.m.r. as 2,2,4,4,5,5,7,7-octamethyloctane; n.m.r. proton ratios for methylene:terminal methyl:internal methyl are calcd. as 2:9:6. An average of six integrations found 1.8:9:5.3 which is within the experimental error which was larger than usual owing to the overlapping of the methyl peaks and the presence of a few small peaks from an unknown impurity. *Anal.* Calcd. for $C_{16}H_{34}$: C, 84.86; H, 15.14. Found: C, 85.08; H, 15.22.

Analytical samples of 2,2,4,4,5,5,7,7-octamethyloctane were obtained by trapping it from an 11.5-ft. column packed with Hi Vac silicone grease on Gas Chrom C.L.A. maintained at 175°.

In other runs the supernatant solutions immediately following the dissolution of metal were assayed by e.s.r. and found to be 1.8×10^{-3} *M* in a paramagnetic species. Its e.s.r. spectrum consisted of an equispaced triplet of equal intensity, h.c.c. 15.6 gauss. By analogy to *t*-nitrobutane, this species is assumed to be di-*t*-octylnitroxide.

Reaction of *t*-Nitrooctane with Sodium in Ether.—*t*-Nitro- octane (15.9 g., 100 mmoles) was stirred with 2.3 g. (100 mg.-atoms) of sodium in 350 ml. of anhydrous ethyl ether. After dissolution of metal was complete, 24 hr., the supernatant ether solution, prior to any work-up, was analyzed by v.p.c. and found to consist of 0.814 g. (5 mmoles) of unreacted *t*-nitrooctane, 2.09 g. (9 mmoles, 18%) of 2,2,4,4,5,5,7,7-octamethyloctane, 3.45 g. (30

mmoles, 30%) of 2,2,4-trimethylpentane, and 4.0 g. (37 mmoles, 37%) of 2,4,4-trimethylpentene-1. The solid which precipitated during reaction consisted only of sodium nitrite (5.97 g., 87 mmoles); no hydroxide ion was detectable in its aqueous solution.

Gas Chromatographic Analyses.—Analyses were run using known compounds as standards *vs.* appropriate internal standards. For each compound determined, weight ratio *vs.* area ratio was plotted for the standard *vs.* internal standard. These plots were linear. Duplicate v.p.c. runs were reproducible within 2% for each component of the same sample. 2,2,4-Trimethylpentane and 2,4,4-trimethylpentene-1 were determined at 68°, He flow rate 92 ml./min. on a 2-m. 0.25-in. o.d. column packed with Polyglycol 750 supported on Celite 545 using isobutyl alcohol as internal standard. *t*-Nitrooctane and 2,2,4,4,5,5,7,7-octamethyloctane were determined at 175°, He flow rate 92 ml./min. *vs.* *n*-hexadecane as internal standard on a 6-ft., 0.25-in. o.d. column packed with silicone grease supported on Celite 545. The relative retention times are: 2,2,4-trimethylpentane, 0.18; 2,4,4-trimethylpentene-1, 0.26 *vs.* isobutyl alcohol; and *t*-nitrooctane, 0.19; 2,2,4,4,5,5,7,7-octamethyloctane, 0.52 *vs.* *n*-hexadecane.

Reaction of 2-Phenyl-2-nitropropane with Sodium.—2-Phenyl-2-nitropropane (7.8 g., 47.2 mmoles) was stirred with 1.1 g. (47.2 mg.-atoms) of metallic sodium in 125 ml. of glyme until the sodium had all reacted (4 days). At the end of this time, the reaction mixture was transferred to a sintered funnel under nitrogen and filtered under nitrogen. The solid filter cake was washed with a small portion of ether and dried. It contained no organic material and consisted of sodium nitrite as shown by infrared. The solid was dissolved in water and assayed for nitrite and hydroxide ions. The solution contained 38.1 mmoles of nitrite ion, 91% based on consumed starting material, and 3.5 mmoles of sodium hydroxide. The pale yellow neutral filtrate was evaporated *in vacuo* to dryness leaving a semisolid residue. Infrared examination of this residue, unexposed to air or moisture up to this point, showed it to consist largely of bicumyl. A small portion of ice-cold methanol was added to the residue and the crude bicumyl was removed by filtration. After two recrystallizations from methanol, 3.42 g. of bicumyl, 61% based on consumed starting material, was obtained, m.p. 115-117°, reported[37] m.p. 118-119°.

Anal. Calcd. for $C_{18}H_{22}$: C, 90.70; H, 9.30. Found: C, 90.70; H, 9.45.

The combined mother liquors from bicumyl crystallization were vacuum evaporated to yield 1.72 g. of oily residue. An e.s.r. assay of this residue showed it to be 4.6×10^{-3} *M* in a species whose triplet spectrum (h.c.c. 14.9 gauss) is consistent with its formulation as di-*t*-cumylnitroxide. Analysis by mass spectroscopy and comparison with authentic samples showed this residue to consist of 51 wt. % unreacted 2-phenyl-2-nitropropane, 13.8 wt. % 2-phenyl-2-propanol, 13.7 wt. % biphenyl, and 21.2 wt. % of a hydrocarbon, $C_{18}H_{22}$, isomeric with bicumyl. All yields reported in Table II are based on the amount of starting material consumed. In other runs, similar amounts of nitroxide were observed in the initial reaction mixture prior to any work-up.

Reaction of 2,2-Dinitropropane with Sodium.—2,2-Dinitropropane (15.0 g., 110 mmoles) was stirred for 4 days at room temperature with sodium (2.5 g., 110 mg.-atoms) until all the metal had reacted. The reaction mixture consisting of a yellow-brown supernatant solution and darker colored solid was filtered under nitrogen. The filter cake was washed well with small portions of pentane and cyclohexane under nitrogen and dried *in vacuo*. It consisted largely of sodium nitrite and after solution in water was found polarographically to contain 4.87 g. (70.6 mmoles, 63%) of nitrite ion. The glyme filtrate together with the pentane and cyclohexane washes was evaporated *in vacuo* to leave a yellow partially crystalline residue. Infrared examination of this residue showed the presence of 2,3-dimethyl-2,3-dinitrobutane which was isolated by extracting the residue with hot cyclohexane. After several recrystallizations from cyclohexane with charcoal, 1.3 g. (7.4 mmoles, 13%) of 2,3-dimethyl-2,3-dinitrobutane was isolated, m.p. 205-210°, reported[38] m.p. 208-209°. An analytical sample, m.p. 214-215°, was obtained by dissolving a portion of the product in ether and passing it through a small column of alumina.

Anal. Calcd. for $C_6H_{12}N_2O_4$: C, 40.90; H, 6.87; N, 15.90. Found: C, 41.27; H, 7.04; N, 15.41; 15.94.

In other reaction mixtures of 2,2-dinitropropane with sodium in glyme, the initial supernatant was examined prior to further work-up by e.s.r. A triplet spectrum (h.c.c. 14.2 gauss) was observed consistent with the formation of a nitroxide, assigned the structure bis-(2-nitro-2-propyl)-nitroxide by analogy to the reaction of *t*-nitrobutane with sodium.

Polarography and Cyclic Voltammetry.—In view of the use of glyme in the sodium reductions it became necessary to study the polarographic behavior of *t*-nitrobutane and the remaining nitro

(36) F. M. Beringer, M. Drexler, E. M. Gindler, and C. C. Lumpkin, *J. Am. Chem. Soc.*, **75**, 2705 (1953).

(37) M. S. Kharasch and W. H. Urry, *J. Org. Chem.*, **13**, 108 (1948).
(38) L. W. Siegle and H. B. Haas, *ibid.*, **5**, 100 (1940).

compounds in the same solvent. This was done in order to eliminate possible complications arising from the use of different solvents for the polarographic and metallic sodium reductions. Tetra-*n*-butylammonium perchlorate was found to be soluble in glyme giving solutions up to 0.8 M in electrolyte, permitting glyme polarography.[39]

Comparison of the sodium reductions with the electrochemical data indicates that no significant differences between these electron sources exist for the compounds studied.

Two-electrode and three-electrode systems were used to obtain the polarographic results. For the two-electrode systems, utilizing a Leeds and Northrop Electrochemograph Type E, a non-aqueous polarographic cell, designed essentially as described by Kolthoff, *et al.*,[40] was used to obtain polarograms on both aceto-nitrile and glyme solutions. The cell was designed to hold 50 ml. of solution. Decinormal concentrations of tetra-*n*-propyl- and tetra-*n*-butylammonium perchlorates were used as supporting electrolytes for acetonitrile and glyme, respectively. Glyme, saturated with tetra-*n*-butylammonium perchlorate, was added to the reference electrode compartment to provide electrical contact with the glyme solution under examination. With aceto-nitrile solutions, electrical contact was established by partially filling the reference electrode compartment with a portion of the solution being examined. The dropping mercury electrode had the following characteristics in 0.1 M KCl, saturated with air at room temperature and on open circuit: $h = 36.2$ cm., $t = 5.14$ sec., $m = 1.64$ mg./sec., $m^2/st^{1/6} = 1.391$.

The three-electrode polarograph was an all electronic instrument similar to units previously described.[41,42a,b] The triangular voltage wave form used for cyclic voltammetry was obtained from a Hewlett–Packard Model 202A low frequency function generator. Voltammograms were recorded on a Moseley Autograf Model 3S x-y recorder or a Hewlett–Packard Model 130B oscilloscope equipped with a Polaroid camera. Normally a fiber type standard calomel electrode (s.c.e.), isolated from the main solution by an intervening salt bridge making contact through a fine sintered glass disk, was used for experiments of short duration. For longer experiments a Ag–AgNO₃ electrode was used in order to prevent contamination of the solution by water. This reference electrode, consisting of a silver wire in contact with a 0.10 M glyme solution of tetra-*n*-butylammonium perchlorate saturated with silver nitrate, was found to be reversible and stable.[43] Its potential is $+0.627$ v. *vs.* s.c.e. All potentials, however, are reported *vs.* s.c.e. All cyclic polarograms were obtained on a hanging drop mercury electrode constructed by sealing a suitable length of gold wire in unplasticized polyethylene tubing. Only the cross-sectional area of the wire at the end of the tube was exposed. A clean mercury drop obtained from a dropping mercury electrode was suspended from the gold wire tip.

All transfers were carried out in a drybox under an atmosphere of prepurified nitrogen dried with silica gel. Glyme was purified as described in the section on sodium reactions. It was distilled immediately prior to use and transferred to the polarographic cell in the drybox.

In Table II are listed pertinent polarographic data for the several nitro compounds, cumylpotassium, and *t*-butyl halides in glyme. As seen from Fig. 5, the useful range in this solvent extends from $+0.65$ to -2.95 v. *vs.* the s.c.e.

It has been found that values of the diffusion current constant, I_d, of 3.5 to 4.0 in glyme are equivalent to one-electron transfers. These values are very similar to the value of 4 which is equivalent to a one-electron transfer in acetonitrile solutions. This has been determined by a comparison of diffusion current constants of such substances as the *o*-, *m*-, and *p*-dinitrobenzenes, styrene, *trans*-stilbene, anthracene, and others in both solvent systems.

The cyclic voltammograms were obtained by cycling the potential linearly over a 3-v. range. Reference to Fig. 2 and 3 shows that following reduction, oxidation peaks for the nitro anion radials were observed. In addition, an oxidation peak at 0.0 v. was present for each compound. This peak is due to nitrite ion[44] since the cyclic voltammogram of tetra-*n*-butylammonium nitrite showed a peak of identical shape at the same potential. Other oxidation peaks were also present arising from decomposition products formed from initially reduced nitro compound. These peaks remain as yet unidentified. A minimum cycling rate of 0.12

v./sec. (0.02 c.p.s.), Fig. 1, was sufficient to just observe oxidation of the *t*-nitrobutyl anion radical. From this it is estimated that the lifetime of the *t*-nitrobutyl anion radical is 0.1–1 sec. Faster cycling rates, 1.2 v./sec. (0.2 c.p.s.), Fig. 2a, resulted in an increased relative peak height of the *t*-nitrobutyl anion radical. In order to observe a comparable onset of *t*-nitrooctyl anion radical oxidation, the cycling rate had to be increased to 30 v./sec. (5 c.p.s.), Fig. 2b. In similarity to *t*-nitrobutane, faster cycling rates, 60 v./sec. (10 c.p.s.), Fig. 2c, also resulted in an increase of the relative peak height of the *t*-nitrooctyl anion radical. *t*-Nitrocumene and 2,2-dinitropropane showed no evidence of forming an oxidizable anion radical at cycling rates up to 90 v./sec. (15 c.p.s.). These compounds also showed a nitrite ion oxidation peak at all cycling rates. Higher cycling rates than these could not be employed since they resulted in voltammograms whose structural detail is obscured by high charging current. In similarity to *t*-nitrocumene, no oxidation of an anion radical from *t*-butyl iodide in glyme was detectable at cycling rates up to 80 v./sec.

α,α-**Dimethylbenzylpotassium** (*t*-**Cumylpotassium**).—Ether solutions of *t*-cumylpotassium have been prepared previously by the cleavage of *t*-cumyl methyl ether with sodium–potassium alloy.[45a,b] It was required, however, to exclude sodium ion from the solution since its reduction would mask the oxidation wave of the *t*-cumyl anion. The following procedure was therefore employed.

Potassium, 2 g., cut into small pieces, was subjected to high shear stirring for 2 hr. in 200 ml. of freshly distilled glyme. The surface of the metal was bright and the glyme was blue indicating the removal of any impurity which would react with potassium. *t*-Cumyl methyl ether,[45a] 1 ml., was added and the mixture stirred for 1 hr. The deep red solution was transferred with a nitrogen-filled hypodermic syringe directly into an electrolysis cell containing a saturated solution of potassium tetraphenylborate in glyme against a nitrogen flow. Sufficient *t*-cumyl potassium solution was added to give a persistent red color to the solution in the cell. The concentration of the *t*-cumyl anion was not known, but is estimated to be about 10^{-3} M. The red color of the solution faded after about 1 hr. As the color faded, the current due to the *t*-cumyl anion oxidation decreased until, when the solution was colorless, no wave due to anion oxidation could be seen. The color of the *t*-cumyl anion was instantly discharged when it was added to solutions containing tetra-*n*-butylammonium perchlorate. Attempts to use other supporting electrolytes containing perchlorate ion failed owing to the precipitation of insoluble potassium perchlorate, resulting in solutions having resistances too high for useful measurements.

Tetra-*n*-butylammonium Nitrite.[46]—A column of 19 ml. of Dowex-X4 cation-exchange resin in equilibrium with aqueous glyme (69 vol. % glyme) cooled to $-20°$ was treated with sodium nitrite (0.5 g., 0.007 mole) in 25 ml. of aqueous glyme followed by elution with 50 ml. of aqueous glyme. All operations were conducted at $-20°$. The effluent from the column was passed directly into a stirred solution of tetra-*n*-butylammonium hydroxide (0.007 mole) in glyme. The solvent was evaporated to dryness and the last traces of moisture removed by azeotropic distillation with benzene. The dry benzene solution was decolorized with charcoal, filtered, and the nitrite precipitated with hexane. The oil which separated soon crystallized and was filtered under nitrogen. The infrared spectrum was identical with that of tetra-*n*-butylammonium bromide except for additional bands at 2510 (vw), 1235–1240 (vs), 799 (w) cm.⁻¹ attributed to nitrite anion; titrimetric analysis of NO_2^-: calcd. 15.97, found 14.09; calculated purity, 88.4%.

Electron Spin Resonance Measurements.—All measurements were made on a Varian V-4500 spectrometer with modulation frequencies of 400 c.p.s. or 100 kc.p.s. For the reaction of *t*-nitrobutane with sodium, a 23-cm. piece of 4-mm. Pyrex tubing sealed to a 23-cm. length of 10-mm. tubing was used. The combined tube was flamed under vacuum, cooled under nitrogen, and a sliver of clean metallic sodium was introduced into the 4-mm. section under a stream of nitrogen. Anhydrous solvent, approximately 5 ml., was then introduced followed by 0.5 g. of *t*-nitrobutane. The nitrogen stream was discontinued and the tube evacuated till the solvent began to boil. The contents were degassed by freeze-thawing several times and the tube sealed. *t*-Nitrobutyl anion radical and di-*t*-butylnitroxide were visible above the metal surface as soon as the tube warmed up sufficiently to be placed in the spectrometer cavity.

Electrolyses were performed in the microwave cavity of the e.s.r. spectrometer using the technique of Geske and Maki.[47] For electrolyses in acetonitrile, tetra-*n*-propylammonium perchlorate was the supporting electrolyte and a calomel reference electrode was used to set the working voltage of the cathode to

(39) W. H. Jura, W. G. Hodgson, and A. K. Hoffmann, Abstracts, 140th National Meeting of the American Chemical Society, Chicago, Ill., September 3–8, 1961, p. 16B.

(40) I. M. Kolthoff and J. F. Coetzee, *J. Am. Chem. Soc.*, **79**, 870 (1957).

(41) D. D. DeFord, Division of Analytical Chemistry, 133rd National Meeting of the American Chemical Society, San Francisco, Calif., April, 1958.

(42) (a) M. T. Kelley, D. J. Fisher, and H. C. Jones, *Anal. Chem.*, **31**, 1475 (1959); (b) *ibid.*, **32**, 1262 (1960).

(43) The concentration of the supporting electrolyte in the reference electrode compartment is important because of its influence on the solubility of AgNO₃ in glyme.

(44) This peak is thought to be due to oxidation of mercury to form a nitrite complex or salt rather than the direct oxidation of nitrite ion.

(45) (a) K. Ziegler and B. Schnell, *Ann.*, **437**, 222 (1924); (b) G. A. Russell, *J. Am. Chem. Soc.*, **79**, 3871 (1957).

(46) The procedure for preparing nitrous acid was developed by Dr. C. S. Scanley of these laboratories [*ibid.*, **85**, 3888 (1963)].

(47) D. H. Geske and A. H. Maki, *ibid.*, **82**, 2671 (1960).

correpond 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 μa. was passed through the cell. Observations were also made with voltages such that 10 and 20 μa. 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-μa. level and more clearly at the 10- or 20-μa. 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.[48,49] 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 μa., 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.

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

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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, $(t\text{-}C_4H_9)_2NO_2^-Na^+$. 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.[1,2] 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[3] 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.

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(2) A. K. Hoffmann, W. G. Hodgson, and W. H. Jura, *ibid.*, **83**, 4675 (1961).

(3) A. K. Hoffmann, W. G. Hodgson, D. L. Maricle, and W. H. Jura, *ibid.*, **86**, 631 (1964).

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[a]

PRODUCTS FOUND IN THE SUPERNATANT PHASE FROM THE REACTION OF t-NITROBUTANE WITH ONE EQUIVALENT OF SODIUM

Product	Run I, mmoles	Run II, mmoles
$i\text{-}C_4H_8$[b]	12.0	7.8
$t\text{-}C_4H_9OH$	3.8	2.2
$t\text{-}C_4H_9ONO_2$	3.7	2.3
$t\text{-}C_4H_9NO_2$	13.5	17.6
$(t\text{-}C_4H_9)_2NO\text{-}t\text{-}C_4H_9$	18.8	12.7
$(t\text{-}C_4H_9)_2N \doteq O$	c	c
$t\text{-}C_4H_9NH_2$	d	d

[a] In these runs 390 mmoles of t-nitrobutane was used. [b] 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. [c] E.s.r. assays showed concentrations of di-t-butylnitroxide of approximately 0.06 mmole. [d] 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.