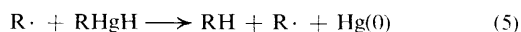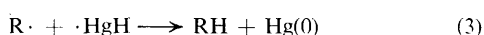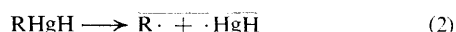# Reactions of Alkylmercuric Halides with Sodium Borohydride in the Presence of Molecular Oxygen[1]

Craig L. Hill and George M. Whitesides*

Contribution from the Department of Chemistry,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.
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Abstract: Reaction of alkylmercuric halides with sodium borohydride in dimethylformamide saturated with molecular oxygen produces alcohols and borate esters in good yields. The products obtained following reaction of neophylmercuric bromide (1), 1,7,7-trimethylbicyclo[2.2.1]heptyl-2-mercuric bromide (9), and *endo-* and *exo-*norbornyl-2-mercuric bromides (13 and 14) with borohydride in the presence of oxygen are compatible with a reaction mechanism involving free, noncaged, alkyl radicals as intermediates. This mechanism finds further support in the observations that reaction of 1 with borohydride and oxygen in solutions containing 2,2,6,6-tetramethylpiperidoxyl radical leads to good yields of the product of coupling of neophyl radical with the nitroxyl. Reaction of α-alkoxyl alkylmercuric halides with borohydride and oxygen generates α-alkoxyl alcohols in good yields; similar reaction of α-hydroxy alkylmercuric halides does not lead to vicinal diols.

Alkyl radicals are established intermediates in the reductive demercuration of alkylmercuric halides by metal hydrides.[2-4] The loss of stereochemistry that occurs during conversion of the carbon–mercury bonds of diastereomeric 2-norbornylmercury compounds into carbon–hydrogen bonds, the characteristic structural rearrangements that accompany demercuration of nortricyclylmercury compounds, and the absence of 1,-2-phenyl migration on reduction of neophylmercuric bromide combine to define the lifetimes of the intermediate alkyl radicals in these reactions to be short, but do not differentiate between radical–cage mechanisms (of which one possible sequence is represented by eq 2 and 3) and rapid radical–chain reactions (eq 4 and 5).

$$RHgBr \xrightarrow{\text{MH}} RHgH \qquad (1)$$

$$RHgH \longrightarrow R\cdot + \cdot HgH \qquad (2)$$

$$R\cdot + \cdot HgH \longrightarrow RH + Hg(0) \qquad (3)$$

$$RHgH \longrightarrow R\cdot \qquad (4)$$

$$R\cdot + RHgH \longrightarrow RH + R\cdot + Hg(0) \qquad (5)$$

Since alkylmercuric halides are among the most readily available and most tractable of organometallic compounds,[5,6] and since their reductive demercuration is a particularly facile process, the reaction of alkylmercuric halides with metal hydrides seems potentially attractive as a method of generating alkyl radicals both for mechanistic studies and for possible utilization in

synthesis, provided that these alkyl radicals survive sufficiently long to be accessible to reagents present in their solutions. One previous attempt to trap alkyl radicals produced during reductive demercuration lead to ambiguous results: reaction of 2-norbornylmercuric bromide with sodium borohydride in the presence of high concentrations of di-*tert*-butylnitroxyl (DTBNO) produced approximately 20% of *N,N*-di-*tert*-butyl-*O*-2-norbornylhydroxylamine.[2] This yield is lower than that expected for reaction between free 2-norbornyl radicals and DTBNO by analogy with other reactions involving this or similar scavengers,[7,8] but steric hindrance may contribute to the apparent inefficiency of the coupling reaction in this instance. This paper describes experiments intended to establish conditions under which alkyl radicals, generated from alkylmercuric halides by reaction with sodium borohydride, can be diverted from the normal path leading to hydrocarbon by an external reagent. Molecular oxygen was chosen as radical scavenger in these experiments for several reasons: it is highly reactive toward alkyl radicals[9] but relatively unreactive toward organomercury compounds[5] and borohydride ion; it has small steric requirements; and its successful coupling with alkyl moieties derived from organomercury reagents, particularly those synthesized by oxymercuration, would provide useful new methods of forming carbon–oxygen bonds and of adding functionality to olefinic moieties. These experiments were also intended to help to differentiate between the two types of mechanistic schemes outlined by eq 2–5, by qualitatively establishing the rapidity with which the generation and

(1) Supported by the National Institutes of Health, Grants No. GM-16020 and HL-15029, and by the National Science Foundation, Grant No. GP-28586X.

(2) G. M. Whitesides and J. San Filippo, Jr., *J. Amer. Chem. Soc.*, **92**, 6611 (1970).

(3) G. A. Gray and W. R. Jackson, *J. Amer. Chem. Soc.*, **91**, 6205 (1969); D. J. Pasto and J. Gontarz, *ibid.*, **91**, 719 (1969).

(4) Reduction using other reagents may take an unrelated course: *cf.* F. R. Jensen, J. J. Miller, S. J. Cristol, and R. S. Beckley, *J. Org. Chem.*, **37**, 4341 (1972).

(5) L. G. Makarova and A. N. Nesmeyanov, "Methods of Elemento-Organic Chemistry," Vol. 4, North-Holland Publishing Co., Amsterdam, 1967; L. G. Makarova, "Organometallic Reactions," Vol. 1, E. I. Becker and M. Tsutsui, Ed., Wiley-Interscience, New York, N. Y., 1970, p 119 ff; Vol. 2, p 335 ff.

(6) W. Kitching, *Organometal. Chem. Rev.*, **3**, 35 (1968); W. Kitching in "Organometallic Reactions," Vol. 3, E. I. Becker and M. Tsutsui, Ed., Wiley-Interscience, New York, N. Y., 1972, p 319 ff.

(7) J. R. Thomas and C. A. Tolman, *J. Amer. Chem. Soc.*, **84**, 2930 (1962); S. F. Nelson and P. D. Bartlett, *ibid.*, **88**, 143 (1966).

(8) Butyl radicals, generated by reaction of *n*-butyl(tri-*n*-butylphosphine)silver(I) with 2,2,6,6-tetramethylpiperidoxyl (TMPO), are scavenged almost quantitatively by this nitroxyl radical in ether solution when [BuAgPBu₃]₀ = 0.05 *M* and [TMPO]₀ = 0.05 *M:* P. E. Kendall, D. E. Bergbreiter, and G. M. Whitesides, unpublished work. Butyl radicals produced by photolysis of di-*n*-butylbis(triphenylphosphine)-platinum(II) are scavenged with high efficiency by DTBNO: G. M. Whitesides, J. F. Gaasch, and E. R. Stedronsky, *J. Amer. Chem. Soc.*, **94**, 5258 (1972).

(9) The rate constants for reaction of alkyl radicals with oxygen are >10⁷ l. mol⁻¹ sec⁻¹: *cf.* B. Smaller, J. R. Remko, and E. C. Avery, *J. Chem. Phys.*, **48**, 5174 (1968); A. A. Miller and F. R. Mayo, *J. Amer. Chem. Soc.*, **78**, 1017 (1956); C. M. Bamford and M. J. S. Dewar, *Proc. Roy. Soc., Ser. A*, **198**, 252 (1949).
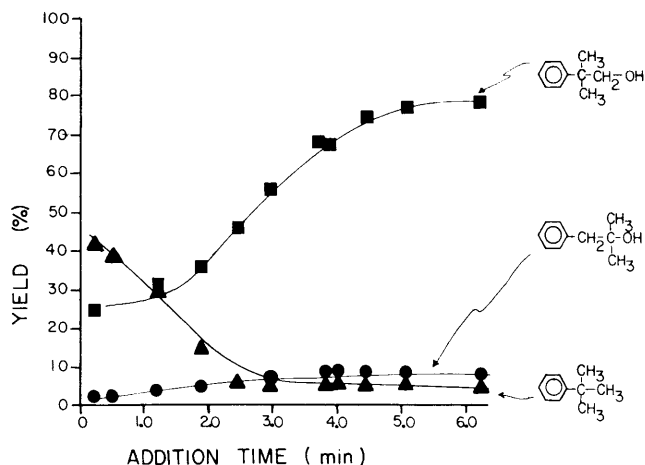
Figure 1. Product yields from reaction of neophylmercuric bromide (1) with sodium borohydride in the presence of oxygen as a function of the addition rate of 10 ml of a 0.05 M solution of 1 to a 0.23 M solution of borohydride in dimethylformamide: (■) yields of neophyl alcohol (2); (●) yields of benzyldimethylcarbinol (3); and (▲) yields of *tert*-butylbenzene. Oxidations were carried out using 0.5 mmol of 1 and 0.7 mmol of sodium borohydride.

Figure 2. Product yields for reaction of neophylmercuric bromide (1) and *trans*-2-methoxycyclohexylmercuric bromide (5) with sodium borohydride in the presence of oxygen, as a function of borohydride. Yields of products are represented by: (□) neophyl alcohol (2); (○) benzyldimethylcarbinol (3); (△) *tert*-butylbenzene (4); (■) *trans*-2-methoxycyclohexanol (6); (●) *cis*-2-methoxycyclohexanol (17); (▲) cyclohexyl methyl ether (8).

consumption of radical intermediates in reductive demercuration occurs.

Results

Products. Initial experiments established that the reaction of alkylmercuric halides with sodium borohydride in dimethylformamide solution in the presence of molecular oxygen does yield alcohols as significant products. Using similar reaction conditions, the organomercury compounds were sensibly inert to oxygen in the absence of borohydride ion. The mercury-(II) originally present in the organomercury reagent is reduced to mercury(0) in high yield during reduction in the presence of oxygen, as it is during reductions in the absence of oxygen.

The reaction conditions used in the major part of the work reported in this paper are based on the results of investigations of the influence of solvent, order and rate of addition of reagents, and work-up procedure on the yield of these alcohols. A number of dipolar aprotic solvents both dissolved and were chemically inert to sodium borohydride and alkylmercuric halides: DMF rather than dimethyl sulfoxide or hexamethylphosphoramide was selected for use on the basis of cost and convenience of purification and removal in work-up. Reactions were carried out by adding a solution of alkylmercuric halide in DMF at room temperature to a solution of sodium borohydride in DMF through which a stream of oxygen was passed rapidly; comparable results were obtained by adding a solution of sodium borohydride to an oxygen-saturated solution of organomercury compounds. The rate of addition of the solution of alkylmercuric halide to the oxygen-saturated borohydride solution significantly influenced the partitioning of products between alcohol and hydrocarbon; representative data used to define reaction conditions are summarized in Figure 1 for the conversion of neophylmercuric bromide (1) to a mixture of neophyl alcohol (2), benzyldimethylcarbinol (3), and *tert*-butylbenzene (4) (eq 6). Substitution of sodium borodeuteride for sodium borohydride results in similar yields; no deuterium is incorporated into 2. The
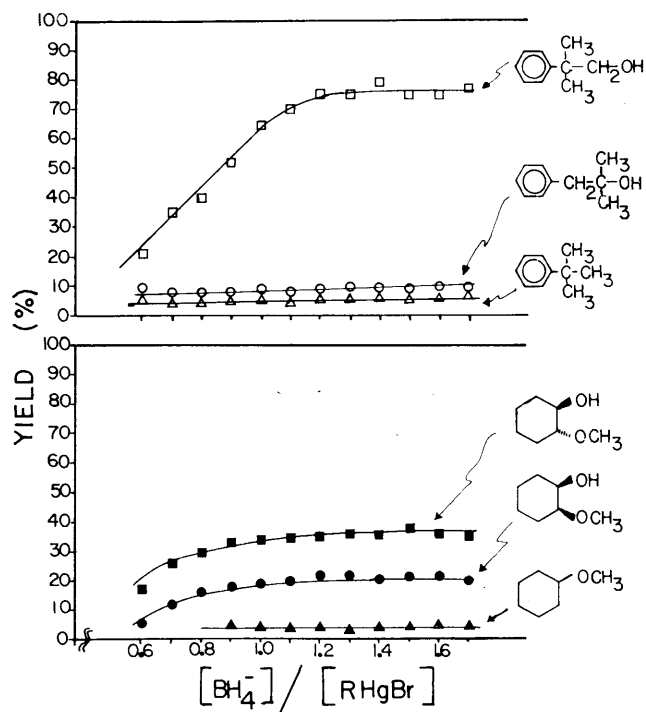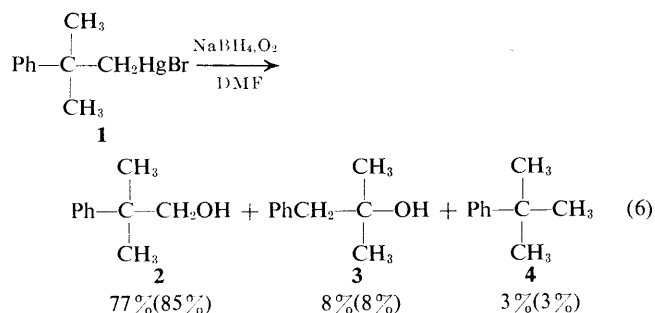
$$
\begin{array}{c}
CH_3 \\
| \\
Ph\!-\!C\!-\!CH_2HgBr \xrightarrow[\text{DMF}]{NaBH_4,O_2} \\
| \\
CH_3 \\
\mathbf{1}
\end{array}
$$

$$
\begin{array}{ccc}
CH_3 & CH_3 & CH_3 \\
| & | & | \\
Ph\!-\!C\!-\!CH_2OH + PhCH_2\!-\!C\!-\!OH + Ph\!-\!C\!-\!CH_3 & (6) \\
| & | & | \\
CH_3 & CH_3 & CH_3 \\
\mathbf{2} & \mathbf{3} & \mathbf{4} \\
77\%(85\%) & 8\%(8\%) & 3\%(3\%)
\end{array}
$$

yields shown without parentheses in eq 6 are those obtained by glpc analysis of the reaction mixture without work-up immediately after addition of the alkylmercuric halide had been completed; the yields in parentheses were obtained by glpc analysis after hydrolysis of the reaction mixture (*vide infra*). Only the former are reproduced in Figure 1. For the concentrations and quantities of reagents typically used in these experiments ([RHgBr]$_0$ = 0.05 M (0.5 mmol), [NaBH$_4$]$_0$ = 0.23 M (0.7 mmol)) the yields of alcohols did not increase if addition of the alkylmercuric halide was carried out over times longer than 6 min. The relative yields of alcohol and hydrocarbon products also depend on the rate of flow of oxygen through the reaction solution: under these conditions, flow rates greater than 200 ml/min maximized yields of alcohol. The effective stoichiometry of the reaction with respect to borohydride was established by examining the yields of products obtained by reaction of typical alkylmercuric halides with varied amounts of borohydride; Figure 2 shows data obtained with 1 and with *trans*-2-methoxycyclohexylmercuric bromide (*trans*-5) (eq 7). In this
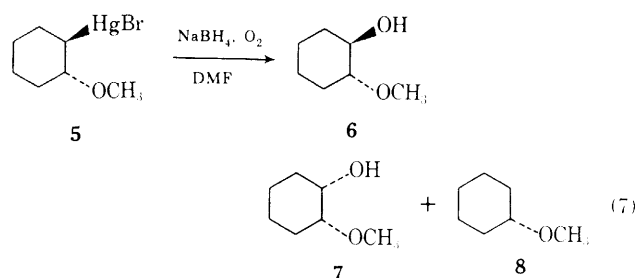
and other instances, 1.2–1.3 mol of borohydride was required to effect complete demercuration of 1 mol of alkylmercuric halide.

In addition to the expected alcohols and hydrocarbons, product mixtures obtained under these reaction conditions contained significant quantities of substances inferred to be alkoxyboron compounds on the basis of their reactivity. The product balance observed when reaction mixtures were analyzed immediately on conclusion of the addition of solutions of alkylmercury reagents to the sodium borohydride solution ranged from 50 to 90%; subsequent hydrolysis reactions increased the product balances to 95–100%. The hydrolysis reactions were carried out either by treating the initial product mixtures with water or aqueous acid, extracting the resulting mixtures with diethyl ether, and analyzing the ethereal phase, or, in many instances, simply by heating the initial product solutions in DMF for several days at ~110°; each of these procedures led to indistinguishable product yields. Representative yields obtained using each of these work-up procedures following the borohydride-induced oxidation and subsequent hydrolysis reactions of 1,7,7-trimethylbicyclo[2.2.1]heptyl-2-mercuric bromide (9) are summarized in eq 8; yields for 1 were summarized in
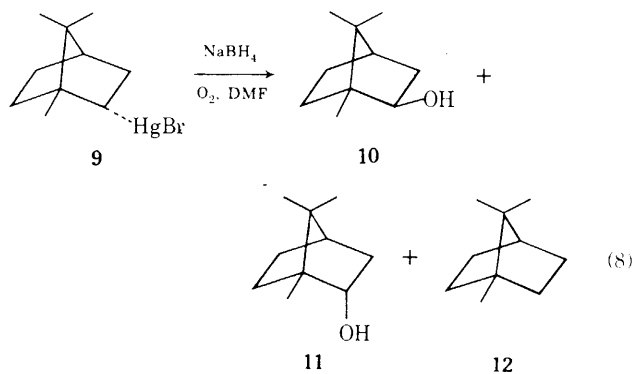
	10	11	12
yields (%) immediately after reaction	41	27	5
yields (%) after hydrolysis (H₂O, rt, 10 min)	60	37	4
(aq H₂SO₄, pH 0, 10 min)	58	36	5
yields (%) after heating (3 days, 110°)	61	36	4

eq 6. The yields in the following section include data obtained both before and after hydrolysis; the differences in these yields suggests the extent to which alkoxyboron compounds are formed in the demercuration reaction.

Detection of Intermediate Free Alkyl Radicals. Free alkyl radicals were established as intermediates using unexceptional stereochemical tests. Demercuration of a mixture of endo and exo diastereomers of 9 in the presence of oxygen led to the corresponding exo and endo alcohols 10 and 11, and 1,7,7-trimethylbicyclo[2.2.1]-

heptane (12) (eq 8); isocamphane and its alcoholic derivatives were not detected among these products. Since Wagner–Meerwein rearrangement is believed to be concerted with formation of a carbonium ion at the 2 position of 9,[10] the absence of rearranged materials among the products of its demercuration indicates that a carbonium ion is not an intermediate in this reaction, but is compatible with a radical intermediate. Similarly, demercuration of 1 in the presence of oxygen yielded a mixture of 2, 3, and 4 (eq 6). Migration of the phenyl group of neophyl radical is a relatively slow process ($k < 10^5$ sec^{-1} at 100°);[11] 1,2-aryl migration in neophyl carbonium is probably concerted with formation of the positively charged center.[12]

Demercuration of endo- and a mixture of endo- and exo-norbornyl-2-mercuric bromides (13 and 14), in the presence of oxygen, yielded the corresponding alcohols exo- and endo-2-norborneol (15 and 16), in addition to small amounts of norbornene (17) and norbornane (18) (eq 9). As previously, the yields without parentheses

	15	16	17	18
	37%(73%)	11%(18%)	9%(11%)	1%(1%)
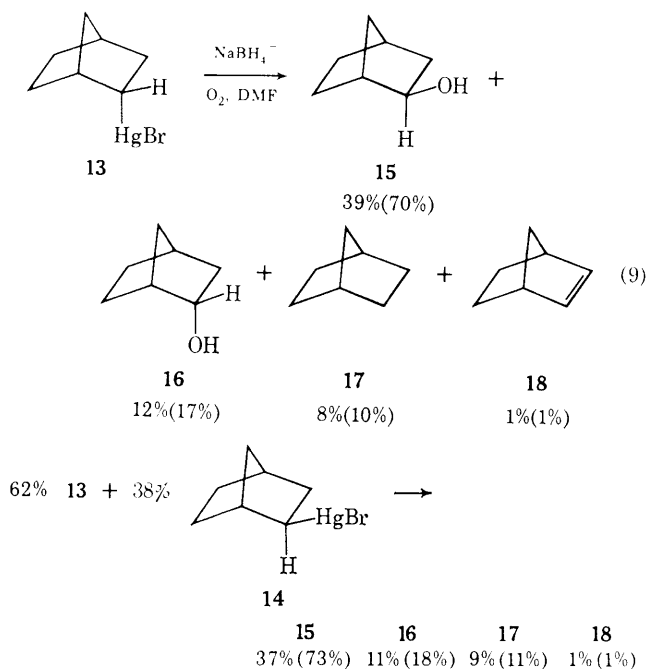
were those obtained at the conclusion of the demercuration reaction; those enclosed in parentheses were obtained after hydrolysis. The oxidation of 13 and 14 occurs with the loss of stereochemistry at C-2 expected to result from an intermediate free 2-norbornyl radical. The ratios of exo to endo alcohol (76:24 from 13 and 77:23 from the mixture of 13 and 14) are within experimental error of one another, and very similar to ratios observed for products from other reactions involving intermediate 2-norbornyl radicals.[2,13,14]

(10) J. A. Berson in "Molecular Rearrangements," Vol. I, P. deMayo, Ed., Interscience, New York, N. Y., 1963, Chapter 3; H. C. Brown and H. M. Bell, *J. Amer. Chem. Soc.*, **86**, 5006 (1964).

(11) R. Kh. Freidlina, *Advan. Free-Radical Chem.*, **1**, 211 (1965); C. Walling in "Molecular Rearrangements," Part I, P. deMayo, Ed., Wiley, New York, N. Y., 1963; C. Rüchart and R. Hecht, *Chem. Ber.*, **98**, 2460, 2471 (1965); G. M. Whitesides, E. J. Panek, and E. R. Stedronsky, *J. Amer. Chem. Soc.*, **94**, 232 (1972); E. J. Hamilton, Jr., and H. Fischer, *Helv. Chim. Acta*, **56**, 795 (1973), and references cited in each.

(12) A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **79**, 1608 (1957); W. H. Saunders, Jr., and R. H. Paine, *ibid.*, **83**, 882 (1961).

(13) P. D. Bartlett, G. N. Fickes, F. C. Haupt, and R. Helgeson, *Accounts Chem. Res.*, **3**, 177 (1970); A. G. Davies and B. P. Roberts, *J. Chem. Soc. B*, 311, 317 (1969); 1815 (1970); R. Schimpf and P. Heimback, *Chem. Ber.*, **103**, 2122 (1970).

To establish that the loss of stereochemistry observed in going from organomercury compounds to products did not reflect epimerization of the mercury reagents under the reaction conditions, pure **13** and a mixture of **13** and **14** were allowed to react to approximately 50% competition, and the remaining organomercury reagents were reisolated. Comparison of the melting point and infrared spectra of recovered and starting material demonstrated that in these reactions, and presumably in the other reactions studied, no loss of stereochemistry in the starting material accompanies reaction. A similar conclusion was reached concerning the analogous reaction in the absence of oxygen.[2]

Taken together, these product studies are entirely compatible with the hypothesis that reductive demercuration of alkylmercuric halides in the presence of molecular oxygen generates intermediate free alkyl radicals, which are trapped in turn by molecular oxygen and converted ultimately to alcohols. These data give no indication that the initial steps in these reactions leading to the intermediate alkyl radicals differ significantly from the corresponding reactions in the absence of oxygen, although small yields of **3** are observed on reduction of **1** in the presence of oxygen while isobutylbenzene was not observed on reduction of **1** in the absence of oxygen.[2] However, they do not define the extent to which the overall reduction–oxidation sequences involves chain or nonchain processes, or details of the involvement of the boron hydride in the reaction. In an effort to resolve these questions, we examined qualitatively the influence of radical inhibitors and of norbornadiene, a scavenger for diborane, on the course of reduction–oxidation of representative alkylmercuric halides.

Reactions in the Presence of Scavengers. The reaction of neophylmercuric bromide (**1**) with borohydride and oxygen was carried out in solutions containing 2,6-di-*tert*-butyl-4-methylphenol,[15] hydroquinone,[15] benzoquinone,[15] and 2,2,6,6-tetramethylpiperidoxyl (TMPO).[16] Very high concentrations of these scavengers slowed but did not stop generation of alcohol. Thus, under conditions in which reaction of **1** with borohydride and oxygen led to **2** (77%), **3** (8%), and **4** (3%), reaction of a mixture composed of **1** and 0.2 equiv of 2,6-di-*tert*-butyl-4-methylphenol yielded **2** (30%), **3** (3%), and **4** (10%); similar results were obtained with hydroquinone and benzoquinone. These observations indicate that the conversions of alkylmercuric halides to alcohols are relatively insensitive to free radical chain inhibitors, and suggest that any chain component in these reactions must involve short chain lengths, or that chain initiation is sufficiently facile that

it is possible to vary the chain length widely without grossly influencing the character of the reaction. It seems more probable that the reaction either involves short chains or no chains.

In a related experiment, reaction of a mixture of **1** and 9.6 equiv of TMPO with borohydride and oxygen generated **19**, the substance expected to result from coupling of neophyl radical and TMPO (eq 10), in good

$$1 + TMPO \xrightarrow[\text{DMF}]{\text{NaBH}_4, O_2} 2 + Ph\text{—}C\text{—}CH_2\text{—}O\text{—}N \quad (10)$$

$$5\% \qquad 19 (95\%)$$
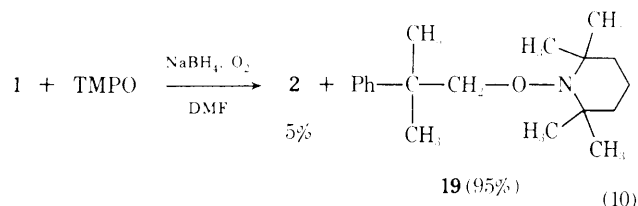
yield.[17] This observation established that essentially all of the radicals produced by reaction between **1** and borohydride ion can be scavenged, and indicates that neither the conversion of **1** to the alcohols **2** and **3** nor its conversion to **4** can be cage reactions.[20]

Norbornene has been used effectively to trap the diborane produced on reaction of borohydride ion with alkylpalladium(II) halides.[21] Reaction of **9** and of a mixture of **13** and **14** with borohydride and oxygen in the presence of large excesses of norbornadiene (20 mol per mol of alkylmercuric halide) resulted in only *ca.* 6% decrease in the yields of the corresponding alcohols. Thus, the course of the reaction is also relatively insensitive to the presence of materials that might compete with the alkylmercuric halides for any diborane present. For comparison, reaction of **1** with 1.2 equiv of BH_3–THF in DMF in the presence of oxygen under reaction conditions similar to those used for reductions with borohydride yielded **2** (20–30%), **3** (<5%), and **4** (50–60%). These results are unfortunately not very informative mechanistically. The observation that the presence of norbornadiene does not significantly alter the product distribution does not necessarily indicate that diborane or complexes of BH_3 with DMF are not effective hydride donors toward alkymercuric halides under the reaction conditions, but only if these or other diborane derivatives are important in these reductions, they must have reactivity toward alkylmercuric halides that is at least comparable with their reactivity toward norbornadiene. Correspondingly, the fact that neophyl alcohol is produced on reaction of BH_3 with **1** in the presence of oxygen does not necessarily imply that the rate of reduction of **1** by BH_3 is sufficient to

(14) The predominantly exo oxidation in these reactions is in agreement with the expectation that 2-norbornyl radical should react with oxygen more readily from the exo side; *cf.* D. I. Davies and S. J. Cristol, *Advan. Free-Radical Chem.*, **1**, 155 (1965).

(15) K. U. Ingold, *Chem. Soc., Spec. Publ.*, No. **24**, 285 (1970); William A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, Chapter 21; C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, pp 162–178, 430–436; K. U. Ingold, *Chem. Rev.*, **61**, 563 (1961); L. Reich and S. S. Stivala, "Autoxidation of Hydrocarbons and Polyolefins," Marcel Dekker, New York, N. Y., 1969, Chapter 3, and references cited in each.

(16) Sterically hindered nitroxyl groups are believed to be stable toward hybridic reducing agents and molecular oxygen; *cf.* A. R. Forrester, J. M. Hay, and R. H. Thomson, "Organic Chemistry of Stable Free Radicals," Academic Press, New York, N. Y., 1968, Chapter 5; E. G. Rozantsev, "Free Nitroxyl Radicals," Plenum Press, New York, N. Y., 1970; D. J. Kosman and L. H. Piette, *Chem. Commun.*, 926 (1969).

(17) In an effort to detect interaction between **1** and TMPO before reaction with borohydride, the esr spectrum of a DMF solution of TMPO ($\sim 10^{-3}$ M) was compared with that of the same solution after addition of **1**; the spectra were not detectably different. Thus, although a number of metal ions have been shown to complex with di-*tert*-butylnitroxyl[18] and TMPO,[19] this and previously reported uv observations[2] suggest that any interaction between stable nitroxyl radicals and alkylmercuric halides is weak.

(18) B. M. Hoffman and T. B. Eames, *J. Amer. Chem. Soc.*, **91**, 5168 (1969); W. Beck, K. Schmidtner, and H. J. Keller, *Chem. Ber.*, **100**, 503 (1967); W. Beck and K. Schmidtner, *ibid.*, **100**, 3363 (1967); B. M. Hoffmann and T. B. Eames, *J. Amer. Chem. Soc.*, **91**, 2169 (1969).
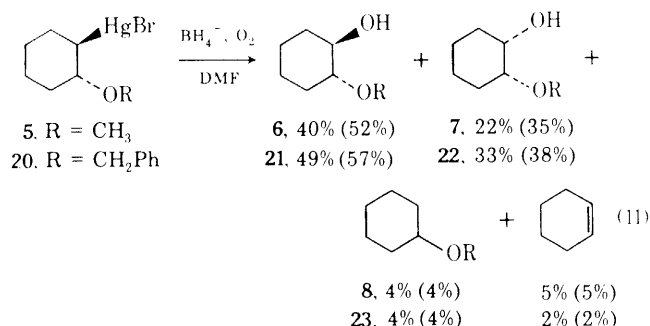
(19) C. M. Paleos, N. M. Karayannis, and M. M. Labes, *Chem. Commun.*, 195 (1970).

(20) The yield of **19** observed also suggests that the relatively low yield (20%) of O-2-norbornyl-N,N-di-*tert*-butylhydroxylamine formed on reduction of **13** or **14** in the presence of DTBNO[2] reflects a steric effect on the coupling reaction, rather than a pronounced cage component to the reaction.

(21) E. Vedejs and M. F. Salomon, *J. Amer. Chem. Soc.*, **92**, 6965 (1970).

compete with reduction of **1** by borohydride ion. Thus, the importance of BH_3 in these reductions is not established by the available data. Nonetheless, the observation that >1.2 equiv of borohydride per equiv of mercurial is required for maximum yield of alcohol (Figure 1) suggests that borohydride rather than diborane or its derivatives is the predominant reductant in these reactions.

Reactions of Oxymercurated Olefins. The most readily accessible class of organomercury compounds are those derived from olefins by oxymercuration and related reactions.[5,6,22] Conversion of alkoxymercurated olefins to β-alkoxy alcohols by reaction with borohydride and oxygen takes place in good yield (eq 11), and appears to offer a convenient method for con-
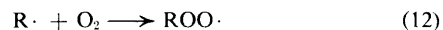

5. R = CH₃   6, 40% (52%)   7, 22% (35%)
20. R = CH₂Ph   21, 49% (57%)   22, 33% (38%)

     8, 4% (4%)   5% (5%)
     23, 4% (4%)   2% (2%)

verting olefins into β-alkoxy alcohols, provided that a diastereomeric mixture of products can be tolerated. Reaction of hydroxymercurated olefins under similar conditions leads to no useful product that we have been able to detect; for example, treatment of *trans*-2-hydroxycyclohexylmercuric bromide with borohydride and oxygen yields cyclohexene (3%), cyclohexanol (4%), and cyclohexanone (5%); the remainder of the product appears as an apparently polymeric material of unknown composition. The factors responsible for the difference in behavior of alkoxymercurated and hydroxymercurated olefins are not readily apparent.

Discussion

Several lines of evidence establish that the production of alcohols by borohydride demercuration of alkylmercuric halides in the presence of oxygen proceeds by intermediate free alkyl radicals. First, the small amount of rearrangement detected during oxidative demercuration of neophylmercuric bromide, and the absence of detectable rearrangement during oxidative demercuration of bornylmercuric bromide, exclude carbonium ion intermediates in these reactions. The involvement of intermediate alkyl carbanions is unlikely, both by analogy with the reaction in the absence of oxygen,[2] and because a carbanion would be expected to react to a detectable extent with DMF. The loss of stereochemistry during conversion of the carbon–mercury bond to carbon–oxygen bonds argues again a concerted process. All of these observations, as well as the significant rearrangement of neophyl moieties to benzyldimethylcarbinyl moieties observed during reaction of **1**, the efficient trapping of neophyl radicals by TMPO, and the slight but detectable inhibition of the reaction of **1** by radical scavengers, are compatible with a reaction course involving generation

(22) N. S. Zefirov, *Russ. Chem. Rev.*, **34**, 527 (1965); R. C. Fahey, *Top. Stereochem.*, **3**, 237 (1968).

and consumption of free, noncaged, alkyl radicals. A plausible reaction sequence for the conversion of alkylmercuric halides to alcohols by borohydride ion in the presence of oxygen would consist of a modification of the sequence involved in the absence of oxygen;[2,23] in these equations "BH" represents a borohydride of unspecified structure. The available data give no indication of the probable source of the hydrogen consumed in reduction of $ROO\cdot$ to $ROOH$; alkylmercuric hydride, borohydride, or solvent (eq 13–15, respectively)

$$RHgBr \xrightarrow{\text{"BH"}} RHgH \tag{1}$$

$$RHgH \longrightarrow R\cdot \tag{4}$$

$$R\cdot + O_2 \longrightarrow ROO\cdot \tag{12}$$

$$ROO\cdot + RHgH \longrightarrow ROOH + R\cdot + Hg(0) \tag{13}$$

$$ROO\cdot \xrightarrow{\text{"BH"}} ROOH \tag{14}$$

$$ROO\cdot \xrightarrow{SH} ROOH \tag{15}$$

$$ROOH \xrightarrow{\text{"BH"}} ROH \tag{16}$$

all seem possible. The observation that >1 equiv of BH_4^- is required to achieve maximum conversion of alkylmercuric halide to alcohol suggests that "BH" in eq 1 must be borohydride ion; the weak influence of norbornadiene on the reaction suggests that diborane is not essential to the reaction scheme. The observation that deuterium is not incorporated into **2** derived from reaction of **1** with sodium borodeuteride indicates that the conversion of $ROOH$ to alcohol takes place by direct reduction of the oxygen–oxygen bond, rather than by base-catalyzed elimination of water from the hydroperoxide with formation of aldehyde or ketone, followed by reduction of this substance by a borohydride (or deuteride).

In conclusion, the treatment of alkylmercuric bromides with borohydride is a mild and convenient way of producing alkyl radicals in solution. If the reaction medium is saturated with oxygen, these radicals can be converted to alcohols in good yield. This method is not necessarily applicable to other classes of reducing agents or organomercury compounds; reductions of vinylic[24] and aromatic[25] mercury compounds follow mechanisms that differ significantly from that followed by alkylmercuric halides and borohydride, and substitution of other reducing agents for borohydride ion may also result in changes in mechanism.[4,23]

Experimental Section

General Methods. Melting points were obtained using a Thomas-Hoover melting point apparatus and are uncorrected. Boiling points are uncorrected. Magnesium sulfate was employed as a drying agent unless otherwise stated. Nmr spectra were run as carbon tetrachloride, carbon disulfide, or dimethyl-d_6 sulfoxide solutions on a Varian T-60 spectrometer; chemical shifts are reported in ppm downfield from tetramethylsilane and coupling constants in hertz. Infrared spectra were taken in sodium chloride cells or as potassium bromide pellets on Perkin-Elmer Models 237 or 237B grating spectrometers. Mass spectra were obtained on a Hitachi Perkin-Elmer Model RMU-6D mass spectrometer. Ana-

(23) Similar conclusions have been drawn concerning the formation of rearranged alcohols in reaction of 2,2,2-triphenylethylmercuric chloride with borohydride ion in the presence of oxygen: R. P. Quirk, *J. Org. Chem.*, **37**, 3554 (1972).

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lytical glpc analyses were performed on F&M Model 810 and Perkin-Model 990 gas chromatographs equipped with flame ionization detectors and Disc integrators. Response factors were obtained with authentic samples. Products were collected for mass spectra by glpc using a Hewlett-Packard Model 700 thermal conductivity instrument with a 12-ft, 20% UC-W98 column operated at 140°. All components in the reaction mixtures could be separated using a 8-ft, 15% Carbowax 20M on Chromosorb W column operated at 120° (for hydrocarbon products) and at 190° for alcohols. Microanalyses were performed by Midwest Microlab, Inc., Indianapolis, Ind.

All demercurations were carried out in reagent grade N,N-dimethylformamide and employed U.S.P. oxygen. Tetrahydrofuran was distilled from a dark purple solution of sodium benzophenone dianion. Pyridine and diethyl ether were distilled from calcium hydride under a nitrogen atmosphere. Mercuric bromide and mercuric acetate were used without purification.

Materials. Benzyldimethylcarbinol (**3**), *tert*-butylbenzene (**4**), isoborneol (**10**), borneol (**11**), norbornene (**18**), norbornane (**19**), norborneols (**15** and **16**), and the cyclohexanediols were commercial samples and were used without purification. Hydroquinone, benzoquinone, 2,6-di-*tert*-butyl-4-methylphenol, and norbornadiene were commercial samples and were purified before use. 1,7,7-Trimethylbicyclo[2.2.1]heptane (**12**, bornane), prepared by hydrolysis of bornylmagnesium bromide, had mp 155–156° (lit.[26] mp 156–157°). 2,3,3 - Trimethylbicyclo[2.2.1]heptane (isocamphane) was prepared by hydrogenating camphene over platinum black in ethyl acetate at 25°. A sample of pure *endo*-bicyclo[2.2.1]heptyl-2-mercuric bromide (**13**), obtained as a gift from D. Bergbreiter, had mp 119–120° (lit.[27] mp 120–121°). Neophylmercuric bromide,[2] 1,7,7-trimethylbicyclo[2.2.1]heptyl-2-mercuric bromide (**9**),[2] bicyclo[2.2.1]heptyl-2-mercuric bromides (**13** and **14**)[2], neophyl alcohol,[28] camphene hydrate,[29] 2-methylcamphenilol,[30] *trans*-2-methoxycyclohexanol (**6**),[31] *cis*-2-methoxycyclohexanol (**7**),[32] *trans*-2-benzyloxycyclohexanol (**21**),[33] and 2,2,6,6-tetramethylpiperidoxyl (TMPO)[34] were prepared using literature procedures. Cyclohexyl methyl ether (**8**), bp 135–136° (lit.[35] mp 135–136°), and cyclohexyl benzyl ether (**23**), bp 70° (0.07 Torr) (lit.[36] bp 88° (0.1 Torr)), were prepared by alkylating sodium cyclohexyl oxide in DMF.

trans-**2-Methoxycyclohexylmercuric Bromide (5).** Methanol (30 ml) containing 24.6 g (0.3 mol) of cyclohexene was added slowly to a stirred suspension of 79.5 g (0.25 mol) of mercuric acetate in 400 ml of methanol. After 15 min the resulting solution became clear. It was treated with 300 ml of 10% aqueous potassium bromide. A white solid precipitated immediately. This solid was recrystallized twice from methanol to yield 75 g (76%) of *trans*-2-methoxycyclohexylmercuric bromide: mp 112.5–113° (lit.[37] mp 114–114.5°); nmr (DMSO-d_6) δ 3.4 (3 H, S), 3.2–3.5 (1 H, broad), 0.9–2.9 (9 H, complex).

Anal. Calcd for $C_7H_{13}BrHgO$: C, 21.35; H, 3.33. Found: C, 21.06; H, 3.50.

trans-**2-Benzyloxycyclohexylmercuric Bromide (20).** To a stirred suspension of 31.9 g (0.1 mol) of mercuric acetate in 150 ml of benzyl alcohol was added 10.1 ml (0.1 mol) of cyclohexene. After 10 min the resulting clear solution was treated with 300 ml (0.1 mol) of warm 0.33 N methanolic sodium bromide. A white precipitate formed over a period of 15 min. After 30 min this precipitate was collected by suction filtration and recrystallized from 3:1 heptane–benzene to yield 37 g (79%) of *trans*-2-benzyloxycyclohexylmercuric bromide: mp 87–88°; ir (KBr pellet) 3030 (m),

2905 (vs), 2850 (s), 1439 (s), 1335 (m), 1155 (m), 1028 (vs), and 737 cm^{-1} (m); nmr (DMSO-d_6) δ 7.4 (5 H, s, aromatic), 4.53 (2 H, s, OCH₂Ar), 3.2–3.6 (1 H, broad singlet, R₂C*H*OR), 0.9–2.8 (9 H, complex).

Anal. Calcd for $C_{13}H_{17}BrHgO$: C, 33.23; H, 3.65. Found: C, 33.37; H, 3.85.

trans-**2-Hydroxycyclohexylmercuric Bromide** (*trans*-**17**). To a stirred suspension of 63.8 g (0.2 mol) of mercuric acetate in 350 ml of water was added 20 ml (0.2 mol) of cyclohexene. The resulting milky mixture was stirred for 15 min and then treated with 200 ml (0.2 mol) of 1 N aqueous sodium bromide solution. A white lumpy solid precipitated immediately. This solid was recrystallized from ethyl acetate to yield 60 g (79%) of *trans*-2-hydroxycyclohexylmercuric bromide: mp 150.5–151.5°; ir (KBr pellet) 3300–3600 (s), 2919 (vs), 2850 (s), 1442 (s), 1349 (m), 1247 (m), 1150 (s), 1102 (m), 1050 (s), 1034 (s), and 950 cm^{-1} (s); nmr (DMSO₃-d_6) δ 4.8 (1 H, s, OH), 3.3–3.9 (1 H, s, methine), 0.9–2.8 (9 H, complex).

Anal. Calcd for $C_6H_{11}BrHgO$: C, 18.97; H, 2.92. Found: C, 18.98; H, 2.89.

cis-**2-Benzyloxycyclohexanol (22)** was prepared by treatment of the monosodium salt of *cis*-1,2-cyclohexanediol with benzyl bromide in DMF. *cis*-1,2-Cyclohexanediol (9.1 g, 78.5 mmol), prepared by the method of Wiberg,[38] was dissolved in 40 ml of DMF. Sodium amide (3.06 g, 78.5 mmol) was added slowly to this stirred solution at 0° over a period of 2 min. After addition was complete, the resulting mixture was maintained under an argon atmosphere, stirred for 40 min, and then treated dropwise with 14.5 g (85 mmol) of benzyl bromide at 0°. The resulting yellow slurry turned gray on heating to reflux temperature. After 2 hr of refluxing, *ca.* 100 g of ice and 100 ml of saturated aqueous ammonium chloride were added to the reaction mixture. The mixture was extracted with four, 100-ml portions of ether. The ethereal phase was dried (MgSO₄), concentrated, and distilled under reduced pressure to yield 11.3 g (55 mmol, 70%) of a clear oil having bp 105° (0.01 mm). Elution with ethyl acetate–hexane (1:5) on a dry column of silica gel isolated *ca.* 0.5 g of pure *cis*-2-benzyloxycyclohexanol (**22**): ir (CCl₄) 3570 (s), 3300–3500 (s), 3059 (m), 3023 (m), 2932 (s), 2851 (s), 1730 (m), 1497 (m), 1450 (s), 1175 (s), and 1080 cm^{-1} (s); nmr (CCl₄) δ 7.40 (5 H, s, aromatic), 4.51 (2 H, s, OCH₂Ar), 3.3–3.9 (2 H, R₂CHO), 2.9 (1 H, broad, OH), and 0.9–2.1 (8 H, complex).

Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.72; H, 8.71.

Procedures for Demercuration in the Presence of Oxygen. Similar procedures were employed in all reactions of organomercury compounds with sodium borohydride in the presence of oxygen. All reactions were carried out at ambient temperature in dimethylformamide solution using 0.50 mmol of alkylmercuric halide, 0.70 mmol of sodium borohydride, and an oxygen flow rate of *ca.* 300 ml/min unless otherwise specified. A representative procedure follows.

Demercuration of Neophylmercuric Bromide (1) in the Presence of Oxygen. Dimethylformamide (3.0 ml) and 0.025 g (0.7 mmol) of sodium borohydride were placed in a 40-ml centrifuge tube which was capped with a No-Air stopper containing a 12-in., 15-gauge stainless steel syringe needle as a vent. Oxygen was supplied to the centrifuge tube from a compressed gas cylinder through a brass needle valve manifold (Metaframe) and four, 8-in., 20-gauge stainless steel syringe needles extending to the bottom of the centrifuge tube. The oxygen flow rate could be regulated precisely by regulating the pressure on the reducing valve at the oxygen tank and the setting of the needle valves on the manifold. Oxygen was bubbled through the solution at a flow rate of ~300 ml/min. The dimethylformamide solution of borohydride was flushed with oxygen for 2 min to saturate the solution and to remove all other gases from the centrifuge tube. Oxidation was accomplished by adding 10 ml of a dimethylformamide solution containing 0.5 mmol of **1** and 0.5 mmol of *n*-pentadecane (an internal glpc standard) dropwise over a 6-min period to the borohydride solution by a syringe equipped with a 6-in., 20-gauge syringe needle inserted through the No-Air stopper. Elemental mercury precipitated over a period of 7 min. Two minutes after addition of the mercurial solution was complete, all the needles were removed from the No-Air stopper and the reaction tube was centrifuged to settle any elemental mercury in suspension. The supernatant was analyzed without further delay by glpc using an 8-ft, 15% Carbo-

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wax 20M on Chromosorb W column operated at 120° for hydrocarbon product and 190° for alcohol product. Hydrolysis of the product mixture was accomplished either by sealing the 40-ml centrifuge tube with the No-Air stopper and placing the sealed tube in an oil bath maintained at *ca.* 110° for 3 days or by adding 6 ml of 1.0 *N* aqueous sulfuric acid to the reaction mixture, and extracting the acidified solution with diethyl ether. The yield of alcohol as a function of the rate of addition of the alkylmercuric halide solution to the borohydride solution was determined by following these general procedures but varying the time involved in the addition of the mercurial solution to the solution of the borohydride. The effective stoichiometry of alcohol production with respect to borohydride ion was determined by following the general procedure but varying the starting amount of sodium borohydride.

Demercuration of Neophylmercuric Bromide (1) in the Presence of Oxygen and 2,6-Di-*tert*-butyl-4-methylphenol and Hydroquinone. The effects of these two inhibitors were determined by following the general procedure except that 0.1 mmol (20 mol % relative to 1) of inhibitor (0.22 g of 2,6-di-*tert*-butyl-4-methylphenol or 0.11 g of hydroquinone) was dissolved in the mercurial solution before the latter was added to the oxygen-saturated solution of the reducing agent. Glpc analysis of the product mixture was carried out after 20 min. After this length of time the reactions carried out in the presence of inhibitor were not yet complete.

O-Neophyl-2,2,6,6-tetramethylpiperid-1-yl Oxide (19). To 20 ml of a tetrahydrofuran solution of 0.3 *N* neophylmagnesium chloride (6.0 mmol) at −50° was added 10 ml of tetrahydrofuran containing 0.63 g (4 mmol) of 2,2,6,6-tetramethylpiperidoxyl. The resulting yellow solution was allowed to warm to room temperature overnight. The resulting light orange mixture was extracted with three 50-ml portions of chloroform. The combined organic phase was washed, dried, and concentrated. Glpc analysis (6-ft, 10% UC-W98 on Chromosorb W column temperature programmed from 100 to 230°) of the resulting red concentrate showed one major peak and several smaller peaks of long retention time, in addition to *tert*-butylbenzene. The major peak was assigned structure 19 on the basis of spectral data: ir (CCl₄) 3080 (w), 3052 (m), 2968 (s), 2930 (s), 2870 (s), 1944 (w), 1871 (w), 1801 (w), 1469 (m), 1372 (m), 1358 (m), 1255 (m), 1245 (m), 1048 (m), 968 (m), and 915 cm⁻¹ (m); nmr (CCl₄) δ 7.3 (5 H, aromatic), 3.70 (2 H, CH₂O), 0.9–1.8 (24 H); mass spectrum (70 eV) *m/e* 289 (<1, M⁺), 274 (<1), 177 (3), 157 (22), 143 (8), 142 (100), 91 (21).

Anal. Calcd for C₁₉H₃₁HO: mol wt, 289.2397. Found: mol wt, 289.2420.

Demercuration of Neophylmercuric Bromide (1) in the Presence of Oxygen and 2,2,6,6-Tetramethylpiperidoxyl. To a solution of 0.5 mmol of 1 and 0.5 mmol of *n*-pentadecane internal standard in 10 ml of DMF was added 0.76 g (4.85 mmol, 9.6-fold molar excess relative to 1) of 2,2,6,6-tetramethylpiperidoxyl. This solution was added to the oxygen-saturated solution of 0.7 mmol of sodium borohydride in the usual manner. Elemental mercury was compacted by centrifugation after 30 min and the red supernatant solution was analyzed directly by glpc (6-ft, 10% on Chromosorb W column temperature programmed from 100 to 230° and an 8-ft, 15% Carbowax 20M on Chromosorb W column operated at 240°).

Demercuration of alkylmercuric bromides in the presence of oxygen and norbornadiene was carried out following the general procedure with 1.01 ml (10 mmol) of norbornadiene (a 20-fold molar excess of norbornadiene relative to alkylmercuric halide) added to the DMF solution of the mercurial before addition of the latter to the oxygen-saturated borohydride solution.