Use of Fragmentation Probes in a Study of the Reduction Reactions of 8-B-4 Complexes

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The reduction of a number of mechanistic probes with several borate complexes, $NaBH_4$, $Li(C_2H_5)_3BH$, and lithium dimesityl borohydride, has been shown to occur by both an electron transfer–hydrogen atom abstraction mechanism and a hydride transfer process. Although the electron transfer–hydrogen atom abstraction mechanism can nearly always be detected or be initiated, it is usually only a minor reaction, and only when the reducing agent and/or the substrate is sterically hindered or when the acceptor is a strong oxidizing agent is the homolytic pathway preferred.

Introduction

Although the mechanism for the reduction reactions of sodium borohydride is generally considered to involve a hydride transfer process,[3] several groups have reported that the reduction of alkyl halides proceeds by a homolytic chain mechanism,[4] see Scheme I. The chain processes

Scheme I

$$RX^{\bullet-} \rightarrow R^{\bullet} + X^- \quad (1)$$

$$R^{\bullet} + BH_4^- \rightarrow RH + BH_3^{\bullet-} \quad (2)$$

$$BH_3^{\bullet-} + RX \rightarrow BH_3 + RX^{\bullet-} \quad (3)$$

were initiated photochemically[4a] or with oxygen (presumably by the formation of a peroxide).[4b]

During the initiated reduction reactions of alkyl halides with tetra-*n*-butylammonium borohydride the EPR spectrum of the intermediate radical anion H_3B^- has been detected.[5]

An EPR study of the reduction of dimesityl ketone with BH_3 reported that the spectrum of the ketyl radical ion was observed. The stable radical is proposed to be the product of electron transfer from the borane.[6]

Boranes (or trialkylboranes) are electronically prohibited from serving as electron donors, whereas "ate" reagents, $R_xBH_y^-M^+$ ($x + y = 4$), are reasonable electron donors. The trialkylboranes are excellent Lewis acids and as such are easily transformed into "ate" intermediates by complexation with donor molecules or ions, and therefore can serve as electron transfer agents.

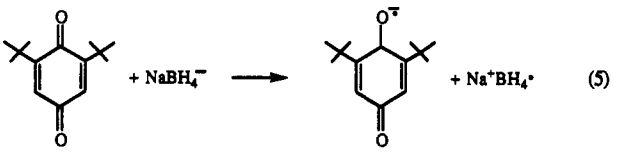
A study by Ashby reported that the reaction of $Li(C_2H_5)_3BH$ (LDEP) with several cyclizable probes (the reduction of 6-haloheptene and 5-halocyclooctene) yielded small amounts of cyclized products diagnostic of homolytic reduction.[7] No chain reduction was reported.[7] Halide reductions using LDEP were previously believed to proceed by a hydride transfer mechanism.[8]

Results and Discussion

Reductions by $NaBH_4$. Treatment of either bromotriphenylmethane, **1**, or 2,6-di-*tert*-butylquinone, **2**, with THF solutions of $NaBH_4$ gives EPR spectra of the persistent trityl radical or the ketyl radical ion of the quinone. It is obvious that under these conditions electron transfer from the "ate" complex to acceptors, **1** or **2**, produced their stable radicals or radical anions, see eqs 4 and 5. The paramagnetic intermediates were characterized

$$Ph_3CBr \rightleftharpoons Ph_3C^+Br^- \quad (\mathbf{1})$$

$$Ph_3C^+ + BH_4^- \longrightarrow Ph_3C^{\bullet} + BH_4^{\bullet} \quad (4)$$



(5)

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by comparison of their EPR spectra with those previously reported.[9]

A fragmentation probe diagnostic of homolytic reduction, the reductive displacement of a *tert*-aliphatic nitro compound,[10] was examined using $NaBH_4$.

The chain mechanism for the homolytic displacement of NO_2^- from a nitroalkane can be classified as either an addition–β-scission or an electron transfer–fragmentation process. Only the activated nitroalkanes appear to follow the latter pathway.[10] 2-(Nitrocyclohexyl)isobutyronitrile, **3**, underwent reduction in acetonitrile or DMF solvent (23 or 61 °C, 48 h) to give 2-(cyclohexyl)isobutyronitrile, **3a** (see Scheme II, eqs 6–8 or 8–10).

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(1) Deceased Oct 30, 1989.

(2) Taken in part from the Ph.D. dissertation of C.-M.Y., University of Alberta, 1991.

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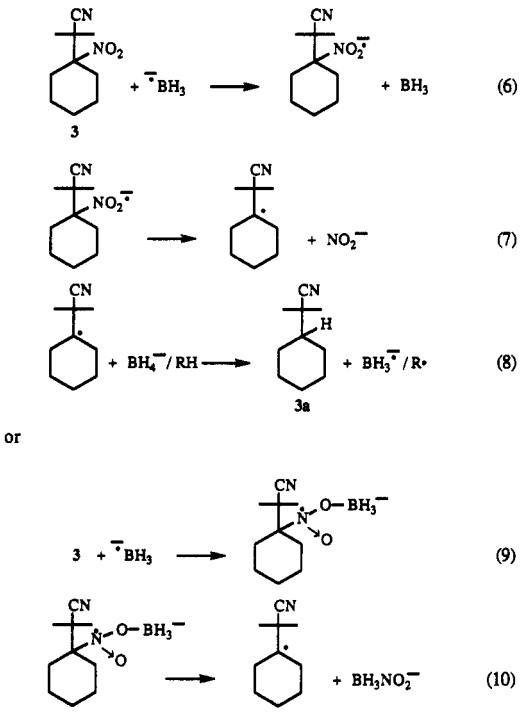
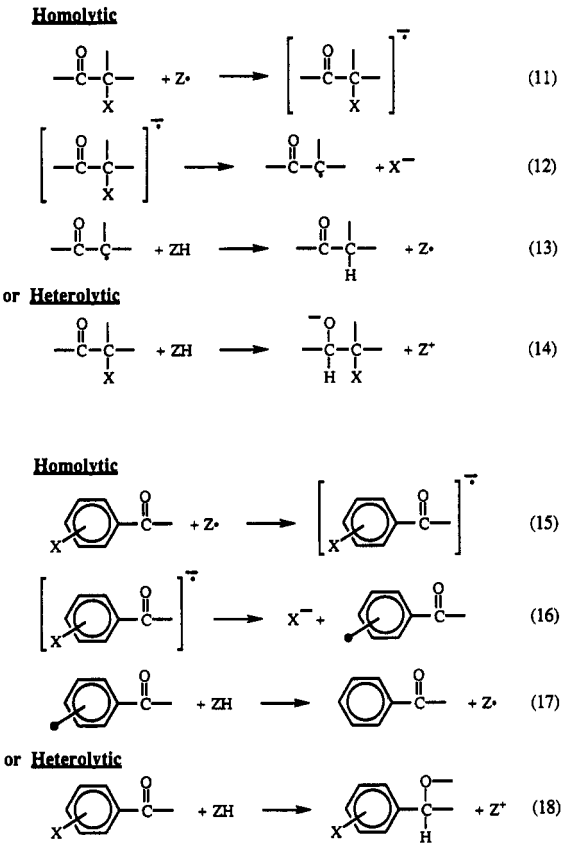
Scheme II



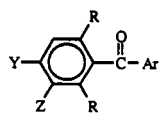
Scheme III



The reaction is typical of a very short chain homolytic process since it could be initiated with a chain length of approximately 6–8 (see Table I, reactions 1 and 2). The yield of reduction product was not affected by molecular oxygen. In order to test the feasibility that a tertiary radical abstracts a hydrogen from BH_4^- (eq 8) the reduction was carried out with $NaBD_4$. Very little (<5%) deuterated **3a** was detected in the product mixture (GC/MS), and although a short chain process is operative transfer of hydrogen must come primarily from the solvent and/or the substrate. Since it was not clear that an electron transfer process was involved in the chain reduction a more definitive reaction was chosen as a diagnostic probe.

α-Halo ketones[11a,b,d,12 b] or ring-substituted aromatic ketones[12a] have been successfully used as mechanistic probes to differentiate between reduction mechanisms which involve either a homolytic electron transfer–hydrogen atom abstraction chain (eqs 11–13 or 15–17) or a heterolytic hydride transfer pathway (eqs 14 or 18),[11] Scheme III.

These probes can be used to differentiate the mechanism qualitatively on the basis of the products formed or quantitatively on the basis of the rates of fragmentation of the intermediate ketyls.[12a,b] The ring substituted aromatic ketones, **4a–c**, were chosen as ketyl fragmentation probes which are amenable for use in the study of the reduction reactions of the 4-B-8 complexes.



4a-c

4a Ar = Ph; Z, R = H; Y = Br
4b Ar = Mes; Z, R = H; Y = Br
4c Ar = 3-Br-Mes; Y, R = CH_3; Z = Br

The sodium borohydride reductions of *p*-bromobenzophenone (**4a**) yield small amounts of the homolytic dehalogenated reduction products when THF solutions of $NaBH_4$ are allowed to react with the halogenated probe; see Table II.

Since homolytic reduction reactions are involved in the reactions of **1–3** and **4a** and since other substrates have also been implicated in borohydride reductions[4,11] a proposal can be made, and tested, that apparently two mechanistic pathways are always open for borohydride reductions, one homolytic and one heterolytic. The major reaction pathway which dominates these competitive reactions is dependent upon the structure of the substrate and/or the reagent; good electron acceptors (**1** and **2**) proceed by the homolytic path while in general most reduction processes proceed by hydride transfer.

For a number of metal hydride reductions Ashby has used as substrates hindered aromatic ketones and mesityl phenyl ketone and dimesityl ketone as chemical probes which, upon electron transfer, give long-lived EPR active ketyl radical ions.[6,13] The rate of reduction of these aromatic ketones is slow,[14] and the homolytic path yields observable paramagnetic intermediates. The observation of EPR spectra during the course of these reactions, however, is not sufficient evidence for the conclusion that the major reduction products are formed homolytically, since both paths are always available and only traces of ketyl radical ions will give persistent EPR absorption.

With the hindered probe, **4b**, reactions of THF/ethanol, THF, and DMF solutions of $NaBH_4$ show products

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Table I. Reduction of 2-Nitrocyclohexylisobutyronitrile with (3) Sodium Borohydride

reactn	$[NaBH_4]/[RNO_2]$	solvent	condns (°C, h)	a (%)	
1	10	CH_3CN	61, 68	10 ± 1	78 ± 2
2	10	CH_3CN	61, 48, 5% AIBN	56 ± 2	21 ± 2
3	5	DMF	61, 48	23 ± 2	69 ± 2
4	5	DMF	61, 48, O_2	20 ± 1	79 ± 1
5	5	DMF	61, 48, 3% AIBN	36 ± 2	54 ± 1
6	5	DMF	61, 48, 5% AIBN	46 ± 2	50 ± 2
7	2.5	DMF	61, 48, 5% AIBN	30 ± 0.5	67 ± 0.5
8	20	DMF	61, 48, 5% AIBN	63 ± 1	35 ± 2
9	5	DMF	61, 48, 5% AIBN, O_2	26 ± 2	65 ± 4
10	10	DMF	61, 48, 10% AIBN	67 ± 1	29 ± 1

[a] GLC yields an average of two to three duplicate reactions. The product is identified by GLC retention times and by a comparison of their GC-IR and GC-MS spectra with those of authentic samples.

Table II. Reduction of Some Bromoaryl Aryl Ketones (4a-c) with $NaBH_4$

substrate	condns (solvent, °C, h)	additives (%)	products, % PhCOPh	PhCH(OH)Ph	p-$BrC_6H_4CH(OH)Ph$	substrate[e] (4a)
4a[a]	THF, 61, 24		trace	2.7 ± 0.3	86.4 ● 4.1	10.9 ± 0.5
		AIBN (6)	trace	4.1 ± 0.5	87.2 ± 4.0	8.7 ± 0.3
	DMF, 61, 24		0.0	2.8 ± 0.2	92.4 ± 3.5	0.0
		AIBN (6)	0.0	39.8 ± 1.9	57.4 ± 2.2	0.0
			PhCOMes	PhCH(OH)Mes	p-$BrC_6H_4CH(OH)Mes$	4b
4b	THF/C_2H_5OH,[b] 23, 24		2.8 ± 0.3	4.8 ● 0.4	91.2 ± 3.9	0.0
	THF/C_2H_5OH, 61, 24	AIBN (6)	3.15 ± 0.2	7.78 ● 0.3	92.77 ± 4.6	0.0
		m-DNB (6)	0.0	2.3 ● 0.3	102 ± 3.8	0.0
	THF, 61, 24		1.1 ● 0.1	0.0	20.5 ± 0.5	78.4 ● 3.7
		AIBN (6)	1.2 ± 0.1	8.6 ± 0.3	16.0 ± 0.4	74.7 ± 3.5
		m-DNB (6)	trace	0.0	18.5 ● 0.3	82.5 ± 4.5
	DMF, 61, 24		3.3 ± 1.9	1.4 ± 0.1	28.2 ± 1.2	66.7 ● 3.4
		AIBN (6)	23.2 ± 1.4	18.1 ● 1.0	26.2 ± 1.7	30.3 ± 2.1
		m-DNB (6)	1.1 ± 0.2	0.5 ± 0.1	31.3 ● 1.9	65.4 ± 3.3
			MesCOMes	3-BromoMesCOMes		4c
4c	DMF,[c] 61, 60		6.6 ± 0.2	12.5 ± 0.4		80.9 ± 3.9
		AIBN (6)	104 ± 6.0	0.0		0.0
		m-DNB (6)	trace	2.36 ± 0.1		95.8 ± 3.7
	C_2H_5OH,[d] 61, 60		0.0	9.6 ± 0.4		92.5 ± 4.5
		AIBN (6)	67.9 ± 1.5	30.7 ± 1.0		0.0
		m-DNB (6)	0.0	0.0		106.0 ± 5.0

[a] [4a] = 0.025 M; $[NaBH_4]$ = 0.072 M. [b] THF/C_2H_5OH = 1/1 v/v. The cosolvent was used to increase the solubility of $NaBH_4$. [c] In DMF, [4c] = 0.0149 M, $[NaBH_4]$ = 0.148 M. [d] In C_2H_5OH, [4c] = 0.0136 M, $[NaBH_4]$ = 0.136 M. [e] Unreacted substrates.

diagnostic of both homolytic and heterolytic reduction pathways. The homolytic dehalogenated products are only formed in minor amounts. Homolytic reduction, however, can be initiated by AIBN and inhibited by small amounts of *m*-dinitrobenzene (DNB); see Table II.

With an even more hindered probe, **4c**, although the reaction is very sluggish, reaction in solvents C_2H_5OH or DMF gives only homolytic reduction products; see Table II.

Reductions by $Na(C_2H_5)_3BH$. When the reductions of **4a–c** were carried out with $Na(C_2H_5)_3BH$ under the same conditions used for $NaBH_4$ the reactions gave almost identical amounts of homolytic reduction; see Table III.

The results listed in Table III are consistent with both of the conflicting studies of the mechanism of $NaB(C_2H_5)_3H$ reductions previously reported.[7,8] The study reported by Ashby[7] concluded that a SET pathway was responsible for the reduction reactions of alkyl halides with $NaB(C_2H_5)_3H$. These conclusions were based on the observation that very small amounts (1–4%), 0 °C; 11%, −78 °C) of cyclized 5-membered ring product were formed during the reduction of 6-iodoheptene and that the trityl radical was observed (EPR) when trityl bromide was allowed to react with a THF solution of $NaB(C_2H_5)H$. The major pathway, however, cannot be defined by the observation that a small amount of a radical-derived product can be detected. In the case of the reductions of **4a** it appears that only very minor amounts of homolytic products are formed. Furthermore, it has been suggested that only a trace amount of radicals can produce cyclized products in these systems by a chain mechanism that does not involve the nucleophilic reagent in the chain-propagating step.[15]

Since the reactions of trityl bromide give an EPR spectrum of the trityl radical with $NaBH_4$ it appears that the borate does undergo SET with very good acceptors (trityl carbonium ion), but since the EPR technique is so sensitive (10^{-7}–10^{-8} M) again only small amounts of the reduction product may be formed by a homolytic pathway.

The reduction of the most hindered ketone, **4c**, with $NaB(C_2H_5)H$ was extremely sluggish, but only homolytic

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Table III. Reductions of Bromoaryl Aryl Ketones (4a-c) with $NaBEt_3H$

substrate	condns (solvent, °C, h)	additives	products, % PhCOPh	PhCH(OH)Ph	p-BrC6H4CH(OH)Ph	substrate[e] 4a
4a[a]	THF, 61, 24		trace	2.3 ± 0.2	88.5 ± 4.2	9.2 ± 0.4
		AIBN (6)	1.4 ± 0.2	2.6 ± 0.2	90.2 ± 3.9	5.8 ± 0.2
		m-DNB (6)	0.0	0.7 ± 0.1	89.4 ± 3.8	9.9 ± 0.8
			PhCOMes	PhCH(OH)Mes	p-BrC6H4CH(OH)Mes	4b
4b	THF,[b] 23, 15		2.0 ± 0.1	4.8 ± 0.3	61.9 ± 3.0	35.0 ± 2.6
	THF, 61, 4		2.4 ± 0.1	8.3 ± 0.8	60.6 ± 3.1	23.9 ± 2.0
	THF,[c] 61, 24		2.4 ± 0.2	10.1 ± 0.4	82.2 ± 3.7	0.7 ± 0.2
		AIBN (6)	2.1 ± 0.1	11.2 ± 0.4	85.7 ± 3.9	0.4 ± 0.2
		m-DNB (6)	0.0	trace	≥99.8 ± 2.0	0.0
			MesCOMes	3-BromoMesCOMes		4c
4c[d]	THF, 23, 24		0.0	3.0 ± 0.2		95.0 ± 3.7
	THF, 23, 22		trace	16.7 ± 1.0		87.7 ± 2.8
		AIBN (6)	0.9 ± 0.1	28.5 ± 2.4		73.8 ± 2.0
		m-DNB (6)	0.0	4.6 ± 1.1		96.5 ± 3.2

[a] [Ketone 4a] = 0.025 M, [$NaBEt_3H$] = 0.50 M. [b] [Ketone 4b] = 0.024 M, [$NaBEt_3H$] = 0.250 M. [c] [Ketone 4b] = 0.024 M, [$NaBEt_3H$] = 0.050 M. [d] [4c] = 0.0046 M, [$NaBEt_3H$] = 0.044 M. [e] Unreacted material.

Table IV. Reduction of $LMBH_2$·2DME with Several Mechanistic Probes (DME, 23 °C)

substrate $PhCOCH_2Cl$	condns (solvent, °C, h)	products (%) $PhCH(OH)CH_2Cl$		$PhCH_2CHO$	SM (%)
	DME 23, 2	40	60	0	0
	1. DME, 23, 2; 2. H_2O, 24 h	0	66	33	0
p-BrC6H5COCH3		p-BrC6H5CH(OH)CH3			
	2 h	79			21
p-BrC6H5COPh (4a)		p-BrC6H5CH(OH)Ph			
	2 h	82			18
p-BrC6H5COMes (4b)		PhCOMes			
	24 h	13			79
	24 h, DNB (1.5%)	0			100
	DMF, 61, 24	4			96
	DMF, 61 °C, AIBN (4%)	32			68

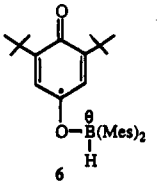
reduction products were detected. The reduction (THF, 61 °C, 22 h) could be initiated with AIBN and inhibited with DNB. No product from hydride transfer was formed.

Although small amounts of radical products are involved in the reduction of most substrates with $NaB(C_2H_5)_3H$, the conclusion reached by Brown[8] that the major pathway for $NaB(C_2H_5)_3H$ reduction involves a hydride transfer reaction is most likely correct. In special cases such as the reduction of an extremely hindered ketone, 4c, the hydride transfer process is so slow that only the homolytic pathway occurs.

Reductions with Lithium Dimesityl Borohydride ($LMBH_2$2DME), 5. Since the more hindered substrates gave more homolytic reduction it was assumed that a more hindered reagent[16] would likewise show more homolytic reduction. As expected, when $LMBH_2$·2DME, 5, was allowed to react with 4b the reaction yielded only homolytic dehalogenation reduction products, see Table IV.

Although the reaction was very sluggish it was shown to proceed via a short-chain radical process since it could be inhibited by a small amount of DNB. The hindered reagent, unlike $NaBH_4$ which reacts with 4b primarily by hydride transfer, gave only products which are diagnostic of an electron transfer–hydrogen atom abstraction process. The radical chain reduction reactions of 5 were further substantiated by carrying out the reductions of 4b in solvent, DMF. At 61 °C the reaction yielded 4% homolytic reduction product, while with small amounts of AIBN (4%), 32% of the radical chain process takes place; see Table IV.

A facile SET process between 5 and 1 or 2 was demonstrated to occur with these good electron acceptors. With 1 a spectrum of the trityl radical was immediately obtained when degassed THF solutions of equimolar amounts of 5 and 1 were mixed in the cavity of an EPR spectrometer. When $LMBH_2$ was allowed to react with a DME solution of 2 the EPR spectra of the spin adduct of 2 was immediately obtained; see Figure 1. The structure of this persistent radical adduct, 6, was consistent with the triplet splitting of the the two quinone hydrogens and the doublet splitting attributed to the hydrogen atom on boron.



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Conclusions

Two reaction manifolds are available for the reduction reactions of borohydrides. The reduction may proceed by both homolytic and heterolytic pathways. Generally, the heterolytic process controls the reductions. Only when the reducing agent and/or the substrate is sterically hindered is a homolytic reduction mechanism followed. However, when the substrate reduced is a very good electron acceptor the homolytic process should be more important.

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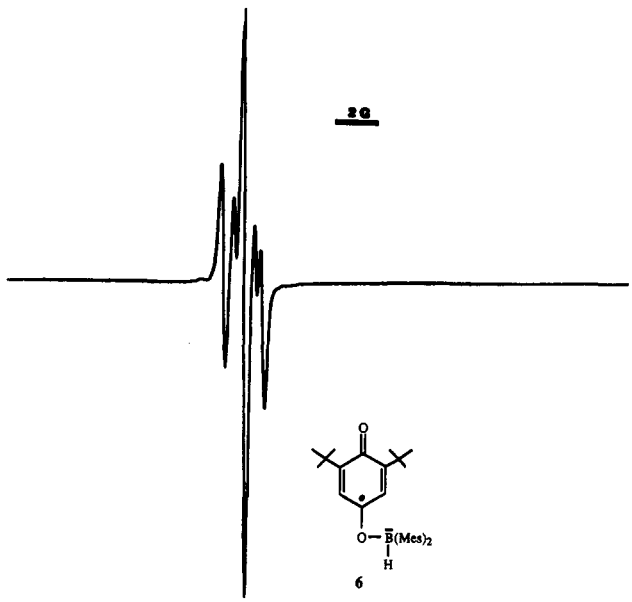

Figure 1. EPR spectrum of the spin adduct of $LMBH_2$·2DME with 2,6-di-*tert*-butylbenzoquinone.

Experimental Section

Instrumentation. ^1H NMR spectra were obtained using either a Bruker AM-400 (400 MHz) or Bruker AM-300 (300 MHz) NMR spectrometer with deuteriochloroform as solvent and residual chloroform (δ 7.24) as an internal lock. EPR spectra were obtained using a Bruker ER200E/SRC spectrometer fitted with a ER4102 ST-Universal X-band resonator operated at 9.6 GHz. The *g* values were determined using a diphenylpicrylhydrazyl external standard. Gas-phase chromatograph–mass spectra (GC/MS) were recorded on a VG-70E mass spectrometer interfaced to a Varian Vista 6000 GC fitted with a DB-1 capillary column interfaced to a 11–250 data system. Gas-phase chromatograph–infrared spectra (GC/IR) were obtained with a HP-5965A IRD spectrometer interfaced to a HP5890 gas chromatograph (Hewlett-Packard) that was fitted with a glass capillary column (Hewlett-Packard ultra 2, 25 m × 0.32 mm × 0.52 μm).

Materials. Tetrahydrofuran (Aldrich, HPLC grade) was dried over KOH and freshly distilled from Na/Ph_2CO. Acetonitrile (Aldrich) was purified by a standard procedure[17] and distilled from CaH_2 before use. Dimethylformamide (Aldrich, HPLC grade) was distilled from CaH_2. Ethanol (Quantum) was distilled from MgO.

2-(Nitrocyclohexyl)isobutyronitrile (**3**) was prepared by the method of Kornblum:[18] mp 108.5–110 °C (lit.[18] 108–109 °C). 2,6-Di-*tert*-butylbenzoquinone (**2**) (Aldrich, 98%) was used as received (mp 65–67 °C). Bromotriphenylmethane (**1**) (Aldrich, 98%) was recrystallized from benzene/petroleum ether, mp 153–154.5 °C (lit.[19] mp 152-154 °C). Anal. Calcd for $C_{19}H_{15}Br$: C, 70.60; H, 4.68. Found: C, 70.83; H, 4.70.

α,α'-Azobis(isobutyronitrile) (Aldrich) was recrystallized from ethanol–water, mp 102 °C (lit.[19] mp 103 °C). *m*-Dinitrobenzene (Fisher) was recrystallized from methanol, mp 91.5–92 °C (lit.[19] mp 88–90 °C). The internal standard for GC, 1,4-di-*tert*-butylbenzene (Aldrich), was recrystallized from ethanol and dried over P_2O_5 in vacuum at 55 °C, mp 78–79 °C (lit.[19] mp 80 °C).

Sodium borohydride (BDH) was recrystallized twice from ethylene glycol dimethyl ether (Aldrich) and dried under vacuum.

$Na(C_2H_5)_3BH$ (Aldrich, 1.0 M solution in THF) was used as supplied.

4-Bromobenzophenone (**4a**) (Aldrich) was recrystallized from ethanol/petroleum ether (30–60 °C), mp 80.5–81.5 °C (lit.[20] mp 80–82.5 °C), Anal. Calcd for $C_{13}H_9OBr$: C, 59.80; H, 3.47. Found: C, 59.60; H, 3.39.

4-Bromo-2′,4′,6′-trimethylbenzophenone (**4b**) was prepared by treating a CS_2 solution of 4-bromobenzoyl chloride with mesitylene in the presence of aluminum trichloride:[21] mp 71.5–72.0 °C (lit.[21] mp 71–72 °C); ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 4H), 6.85 (s, 2H), 2.30 (s, 3H), 2.04 (s, 6H). Anal. Calcd for $C_{16}H_{15}OBr$: C, 63.32; H, 5.05; Br, 26.35. Found: C, 63.38; H, 4.99; Br, 26.35.

3,3′-Dibromo-2,2′,4,4′,6,6′-hexamethylbenzophenone (**4c**) was prepared from dimesityl ketone (3.2 g, 12 mmol), 20 mL of CCl_4, 0.05 g of $FeCl_3$, and a few crystals of I_2. A solution of 1.5 mL of bromine (28 mmol) in 10 mL of CCl_4 was added dropwise while the mixture was stirred at rt. After 1 h, the mixture was heated at reflux for 4 h. The mixture was then diluted with ether and washed with aqueous 10% $NaHCO_3$ solution, 5% sodium thiosulfate, and finally with water. The solvent was evaporated, and white solid was obtained. After flash chromatography (silica gel, 20–45 μm, pH 7.1) using 5:95 diethyl ether/hexane as eluant and subsequent recrystallization, 2.7 g of white crystals was obtained, yield, 52%. The GC showed only one peak. TLC (silica gel, 5:95 v/v Et_2O/hexane) showed one spot: mp 103-104 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 6.90 (s, 2H), 2.36 (s, 6H), 2.25 (s, 6H), 2.00 (s, 6H); HRMS m/z^+ 425.9840 calcd for $C_{19}H_{20}{}^{81}Br_2O$, found 425.9840. Anal. Calcd for $C_{19}H_{20}Br_2O$: C, 53.80; H, 4.75; Found: C, 53.74; H, 4.86.

Lithium dimesityl borohydride bis(dimethoxyethane), $LMBH_2$·2DME, was prepared according to the literature procedure,[16] mp 164–165 °C (lit.[16] mp 164–165 °C).

General Procedure for the Reduction of Substrates and Quantitative GC Analysis of Products. An aliquot of a solution of borohydride (0.05–0.25 M) was placed in one arm of a Pyrex H tube, and an aliquot of a solution of substrate (0.020–0.025 M) containing 1,4-di-*tert*-butylbenzene (with or without the additive AIBN or DNB) in a desired solvent (THF, DMF, CH_3CN, ethanol, or THF/ethanol) was placed in the other arm of the H tube. The tube was degassed under vacuum (three times) and sealed. The two solutions were thermostated at the desired temperature and mixed. The reaction was carried out for the time specified; see Tables I–III. The tube was cooled, opened, quenched with dilute HCl, dried (anhydrous $MgSO_4$), and analyzed by GC.

The product mixture from the reduction of 4-bromobenzophenone (**4a**) was analyzed using a 25 ft × 1/4-in. stainless steel column packed with 10% FFAP on Chromosorb, WAW DMCS, 60/80 mesh. The product mixtures from the reductions of **3**, **4b**, and **4c** were analyzed using a 25-ft × 1/4-in. stainless steel column packed with 10% SE-30 on Chromosorb, WAW DMCS, 60/80 mesh. GC analysis was carried out using a HP5840A gas chromatograph equipped with a hydrogen flame detector interfaced to a HP5840A integrator. The area ratios were converted to mole ratios for quantitative determinations by using standard calibration curves constructed from known mixtures of the authentic materials. Products were identified by a comparison of their retention times and GC–MS and GC–IR spectra with those of authentic materials. The quantitative results listed in Tables I–III are the average results of two or more independent experiments.

EPR Spectroscopy of the Reactions between the Borohydrides and Bromotriphenylmethane or 2,6-Di-tert-butylquinone. A THF solution of bromotriphenylmethane (2.0 mL, 0.02 M) or 2,5-di-*tert*-butylquinone was placed in one of the divided arms of a H tube fitted also with a quartz EPR tube. A second THF solution of the borohydride (2.0 mL, 0.02 M) was placed in the second arm of the H tube. The solutions were degassed three times and then sealed. The solutions were mixed at room temperature, and the filled EPR tube was immediately placed in the cavity of the EPR spectrometer. The EPR spectra were then recorded.

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