The Use of Chemical Probes To Differentiate between Polar and SET–Hydrogen Atom Abstraction Pathways Involved in the Reduction Reaction Promoted by an 8-Al-4 Anion[1]

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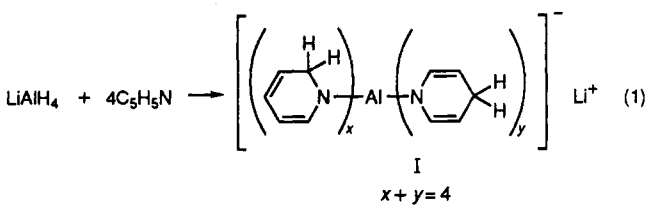
The mechanism for the reduction of aromatic ketones and alkyl halides with lithium tetrakis(*N*-dihydropyridyl)aluminate was found to proceed competitively by hydride reduction and by single electron transfer (SET)–hydrogen atom abstraction processes. A series of ketyl fragmentation probes were used to differentiate the two pathways. A SET process is the dominant pathway when the ketones involved are sterically hindered or when strong electron acceptors are used as the substrates. The observation that EPR-active intermediates can be detected, or that small amounts of radical derived products are formed, demonstrates only that a SET pathway is available but cannot be used to establish the mechanism of the major product-forming reactions.

Introduction

A number of years ago, Lansbury and co-workers reported that a pyridine solution of $LiAlH_4$ (LAH) formed a 1:4 molecular complex, lithium tetrakis(*N*-dihydropyridyl)aluminate (LDPA), see eq 1.[3,4]



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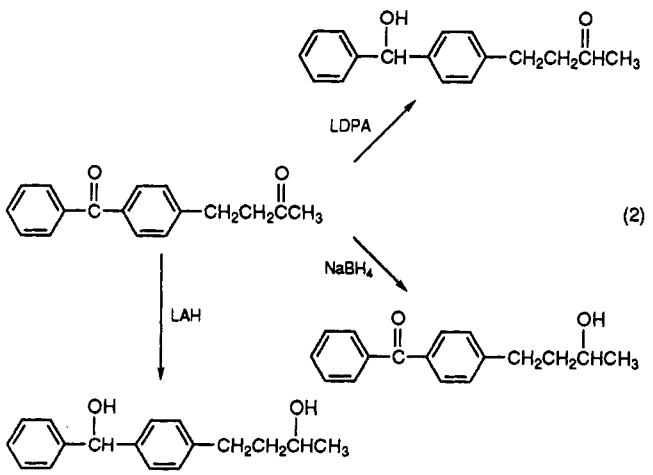
$x + y = 4$

The newly formed reagent was less reactive than LAH when it was allowed to react with organic carbonyl containing substrates.[3] The reagent was more reactive with diaryl ketones than with aliphatic ketones, when its reactivity was compared to the reduction reactions of $NaBH_4$ (see eq 2).[3,5]



The reduction reactions of LDPA were reported to proceed by a polar mechanism in which a hydride is transferred to the substrate from either the 1,2- or 1,4-dihydropyridyl ligand.[5] It was reported that during the LDPA reduction of 4,4′-dichlorobenzophenone no significant difference in the reduction rates was observed from either the 1,2- or 1,4-dihydropyridyl ligands.[5]

Recently LDPA has been proposed as an inorganic analog of the dihydropyridyl moiety of NADH or NADPH.[1] Since model compounds containing a 1,4-dihydropyridyl structure have been shown to react by both homolytic[6,7] and heterolytic pathways[6,8] it was advisable to investigate in some detail the reduction reactions of LDPA. LDPA itself has been reported not only to undergo heterolytic reductions[5] but also to produce, upon reaction with mesityl phenyl ketone, persistent radicals (EPR) by an electron-transfer process.[9]

The use of EPR spectroscopy to differentiate between homolytic and heterolytic pathways has limitations since EPR-active materials can be detected at very low concentrations ($>10^{-7}$ M) and the observation of an EPR spectra is not a conclusive indication that the major pathway involved a homolytic reaction.

The use of α-halo ketones[10,11] or ring-substituted aromatic ketones[11] as mechanistic probes has been successfully used to differentiate between the reduction mechanisms which involve either homolytic electron-transfer–hydro-

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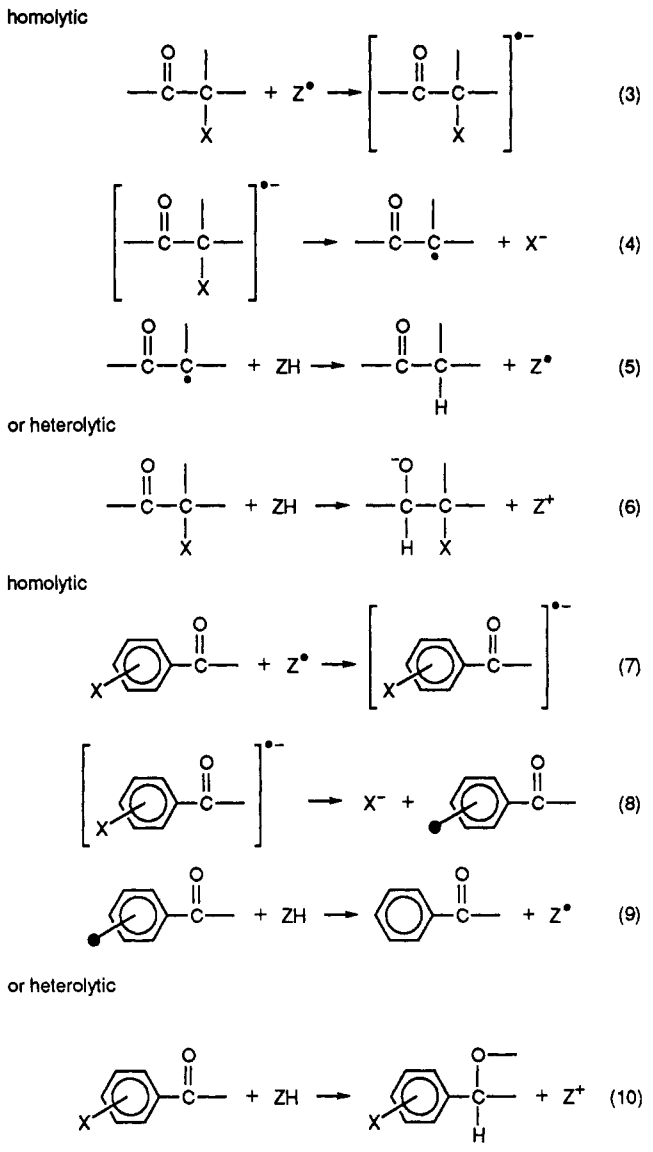
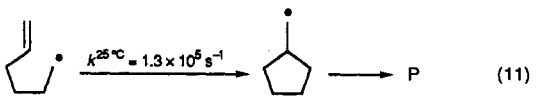
Scheme I



gen-atom-abstraction chain reductions (eqs 3–5, 7–9) or heterolytic hydride-transfer pathways (eq 6 or 10), Scheme I.

Another chemical probe used widely to differentiate between homolytic and heterolytic pathways is based on the cyclization of the 5-hexenyl radical, where products produced from the cyclopentylmethyl radical are indicative of a radical intermediate (eq 11).[12]



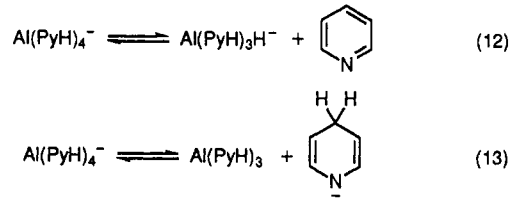
A preliminary report concerning the LDPA reduction of 5-hexenyl iodide stated that cyclized hydrocarbon products that were formed were indicative of the involvement of a SET mechanism.[9] Unfortunately the experimental results obtained from this study have not been published and no details concerning the reduction are available.

Results and Discussion

A number of chemical probes can be used to establish the mechanism of the LDPA reduction of aromatic ketones. When LDPA was allowed to react with benzophenone in the cavity of an EPR spectrometer, no spectra for benzophenone ketyl could be observed. With more hindered ketones, mesityl phenyl ketone (MPK) or dimesityl ketone (DMK), Ashby has reported that the ketyls of both aromatic ketones were almost immediately detected when the ketones were treated with LDPA.[9] Contrary to this report, when LDPA was allowed to react with either MPK or DMK, no EPR spectra could be detected. Only after an extended period of time (MPK, 2 d; DMK, 5 d) was an EPR signal detectable. For DMK a signal of maximum intensity was observed after 24 d while with MPK maximum intensity is observed in 5 d. As previously reported[9] the spectra observed were identical to those of the independently generated lithium ketyls of MPK or DMK, however, the difference in the rates of formation of the radical ions from the aromatic ketone appears to be due to the method of preparation of LDPA. In the present work crystalline LDPA, free from LAH, was used in the spectral studies, since the spectra of the lithium ketyls are immediately generated upon treatment of each ketone with LAH. An analysis of the reaction products from the reaction of the two ketones showed only alcohol is produced (DMK > 40 d) with LDPA. With LAH not only is the ketyl of DMK formed immediately but after 24 h the spectrum of the radical ion had changed to that of the dimesitylmethyl radical.[13] An analysis of the product mixture showed that dimesitylmethane had been produced, a product which is not formed from the LDPA reduction of DMK or dimesitylcarbinol.

From these results it appears that the LDPA reductions of DMK and MPK previously reported[9] were carried out with LDPA that was contaminated with LAH (insufficiently "aged") while the LDPA that is prepared free from LAH (^{27}Al NMR)[4] is much less reactive than LAH.

Since the formation of LDPA is reversible,[4] it is not clear whether the ketyl produced during its reduction was a result of ET from LDPA, from another aluminate complex (eq 12), or from the dihydropyridyl anion (eq



13). Since the equilibrium lies far to the left, electron transfer to form a stable intermediate will be, as observed, extremely slow.

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Table I. Reduction of Diaryl Ketones with LDPA in THF[a]

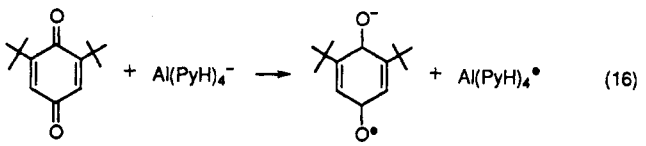
ketone	[LDPA]/[ketone]	conditions	yields, %	recovery of ketone, %
Ph_2CO	1.25	23 °C, 3.5 h	97	none
PhCOMes	11.0	23 °C, 66 h	40.7	61.8
	11.0	61 °C, 66 h	98.8	1.1
Mes_2CO	11.3	23 °C, 10 d	0.0[b]	100
	11.3	61 °C, 66 h	14.3	85.0

[a] All reactions were run in degassed H reaction tubes. [MPK] = 0.0178 M, [DMK] = 0.0129 M, [Ph_2CO] = 0.117 M. [b] Quenched with benzophenone before quenched with water. When the products were analyzed on GC, it is shown that 4.0% of Ph_2CO was consumed to form 3-pyridyldiphenylcarbinol, the structure of which was confirmed by GC/MS and GC/IR upon comparison with authentic sample (prepared independently from methyl ester of nicotinic acid and 2 equiv of lithiobenzene).

With very strong electron acceptors, most likely, LDPA itself can act as an electron donor, since it rapidly reacts with either trityl bromide or 2,6-di-*tert*-butylquinone to give the trityl radical or the quinone radical ion (see eqs 14–16). When the reaction of trityl bromide was quenched

$$Ph_3CBr \rightleftharpoons Ph_3C^+Br^- \quad (14)$$

$$Ph_3C^+ + Al(PyH)_4^- \longrightarrow Ph_3C^\bullet + Al(PyH)_4^\bullet \quad (15)$$



(16)

after 6 h, a 54% yield of triphenylmethane was obtained; no starting material could be detected.

Ketone reductions will be slower the more hindered the substrate, whether LDPA reacts by a SET or a hydride-transfer mechanism. This observation appeared to be qualitatively true when LDPA was allowed to react with benzophenone, MPK, and DMK, see Table I.

The Fragmentation Probe. When excess LDPA is allowed to react with *p*-bromoacetophenone (II) (23 or 61 °C), only the product of heterolytic reduction, 1-(*p*-bromophenyl)ethanol, is formed. The reduction of *p*-bromobenzophenone (III) at 23 °C gives a quantitative yield of *p*-bromobenzhydrol but when the reduction was carried out at 61 °C, 0.6% of the debrominated reduction product benzophenone could be detected. The reduction of the more hindered halo ketones, halophenyl mesityl ketones (IVa-c), with LDPA appears to proceed by both homolytic (dehalogenation) and heterolytic pathways. When the reduction of THF solutions of *p*-bromophenyl mesityl ketone, *p*-BrMPK (IVa), was either carried out at 23 °C or 61 °C the ratio of polar/radical reduction products was approximately 2/1. In the more polar solvent, CH_3CN, homolytic reduction was favored 4-9 times (see Table II). Neither the yield, nor the ratio, of reduction products was affected by an added initiator (AIBN) or inhibitor (DNB). The free radical nature of the dehalogenation process was substantiated by carrying out the LDPA reduction of *p*-BrMPK in a solvent mixture of CH_3CN/*n*-hexene. The trapping products *p*-(*n*-hexyl)phenyl mesityl ketone and its corresponding carbinol were obtained in the product mixture. In this solvent mixture a third product, the dimer of MPK, was also detected, see Table II. With LDPA both mechanisms can conceivably lead to nondehalogenated reduction products if hydrogen atom transfer is in competition with ketyl fragmentation. When the substitution pattern of the halogenated ketone, SM (IVa-c) is changed, the fragmentation rate constants for the halobenzophenone ketyls, $SM^{\bullet-}$ are affected and if there is a competition between fragmentation, k_{fX}, and abstraction, $k_{H^\bullet}$, the ratio of nondehalogenated/dehalogenated, P_N/P_D, reduction products should reflect this change (*i.e.*, the halo ketones with the smallest fragmentation rate constant should give the most halogenated alcohol. The relative ability to accept an electron would, presumably, not be much affected by the change in substitution pattern. Ketyl fragmentation rates, k_{fX}, for halogenated benzophenones have recently been reported.[11] The fragmentation rates are[14] *o*-bromo-:*p*-bromo-:*m*-bromobenzophenone; 10^5 s^{-1}:10^5 s^{-1}:10^3 s^{-1}. A competitive formation of *p*-bromophenylmesitylcarbinol from a ketyl precursor predicts an increase in the ratio, *N*/*D*, of *o*-Br ≈ *p*-Br > *m*-Br, however, since hydride transfer to *o*-bromophenyl mesityl ketone (IVc) should be more sterically hindered than that to MPK itself, although the fragmentation rate is increased, the hydride-transfer rate should be slower. The relative kinetics of formation of the products P_N/P_D can be derived from the equations given in Scheme II, eqs 17–20.

Scheme II

$$LDPA + SM \xrightarrow{k_{H^-}} \rightarrow P_N \quad (17)$$

$$LDPA + SM \xrightarrow{k_e} \rightarrow SM^{\bullet-} \quad (18)$$

$$LDPA + SM^{\bullet-} \xrightarrow{k_{H^\bullet}} \rightarrow P_N \quad (19)$$

$$SM^{\bullet-} \xrightarrow{k_{fX}} \rightarrow P_D \quad (20)$$

Using a steady-state treatment for the concentration of the ketyl, [$SM^{\bullet-}$], two cases can be defined: case 1, (halophenyl)mesitylcarbinol is formed by hydride transfer alone (*i.e.*, $k_{H^\bullet} = 0$); case 2, (halophenyl)mesitylcarbinol is formed by two pathways, hydride transfer (k_{H^-}) and electron transfer–hydrogen atom abstraction (k_e, $k_{H^\bullet}$).

Case 1: where $k_{H^\bullet} = 0$

$$\frac{P_N}{P_D} = \frac{k_{H^-}}{k_e}$$

Case 2:

$$\frac{P_N}{P_D} = \frac{k_{H^-}}{k_e}[a + 1] + a$$

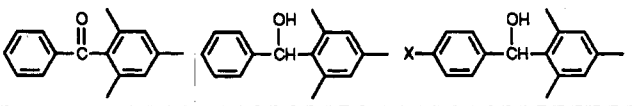
where

$$a = \frac{k_{H^\bullet}}{k_{fX}}[LDPA]$$

The ratio k_{H^-}/k_e should be similar for the meta- and para-substituted benzophenones since the differences in steric effects are negligible and the reduction potentials should be almost the same (E_0 = -1.63 V, *p*-bromobenzophenone; *m*-bromobenzophenone, E_0 = -1.57 V). The ketyl fragmentation rates (k_{fX}), however, are expected to

(14) The fragmentations rates, k_{fBr}, for *m*- and *p*-bromo-substituted benzophenone ketyls have been measured electrochemically. Since the values of k_{fCl} for *o*- and *p*-chlorobenzophenone ketyls only differ by a factor of 2, the value $k_{fo\text{-}Br}$ for *o*-bromobenzophenone ketyl was estimated as 2 × *p*-bromobenzophenone ketyl.

Table II. Reduction of Halophenyl Mesityl Ketones (X-2',4',6'-Trimethylbenzophenones, IVa–c) with LDPA in THF or CH_3CN[a]

ketone (X)	[LDPA]/[ketone]	conditions	yield, % 			starting material
p-Br (IVa)	4.2[b]	THf, 61 °C, 1 h	0.33±0.08	29.0±0.05	75.1±0.1	0.33±0.01
	4.2[b]	THF, 61 °C, 3% AIBN, 11 h	0.26±0.02	29.1±2.9	73.0±1.9	1.0±0.6
	4.2[b]	THF, 61 °C, 3% DNB, 11 h	0.29±0.01	32.8±4.2	70.7±2.2	0.6±0.1
	5.9[c,d]	THF, 23 °C, 29 h	10.0±1.1	3.0±0.3	28.3±1.4	57.0±2.5
	5.9[d]	THF, 61 °C, 3.5 h	0.8±0.1	31.5±2.4	62.2±3.21	trace
	5.7[e]	CH_3CN, 23 °C, 28 h	25.2±1.2	4.4±0.3	3.3±0.2	66.8±3.4
[LDPA] = 0.101	8.3[e]	CH_3CN, 61 °C, 15 h	51.7±0.3	31.8±1.2	18.6±0.1	1.2±0.6
	5.7[f,g]	7.2:1 CH_3CN/*n*-Hexene, 61 °C, 24 h	25.7±1.4	20.1±0.8	28.7±1.2	1.4±0.1
[LDPA] = 0.099	4.2	CH_3CN, 61 °C, 15 h, DCPH 0.35 M, DCPH 0.7 M	0.0	65.3	36.1	0.0
			0.0	60.8	37.3	0.0
m-Br (IVb)	1.9[h]	THF, 23 °C, 14 h	1.1±0.1	0.50±0.31	28.8±5.1	69.8±0.8
	1.9[h]	THF, 61 °C, 14 h	1.7±0.5	16.2±0.4	81.8±3.9	2.1±0.5
	7.9[i]	CH_3CN, 61 °C, 15 h	39.7±2.5	26.2±2.2	31.7±2.6	7.3±2.2
o-Br(IVc)	2.4[j]	THF, 23 °C, 18 h	13.8	5.5	50.6	32.5
	2.4[j]	THF, 23 °C, 6 d	0.5	28.1	69.5	0.50
[LDPA] = 0.101	2.4[j]	THF, 61 °C, 10.5 h	0.6	28.3	68.7	1.74
	9.6	CH_3CN, 61 °C, 15 h	56.9±1.7	35.7±2.1	9.9±1.0	3.2±0.8

[a] All the reactions were run in duplicate in degassed H tubes. All the products were analyzed by GC on 10% SE-30 column and identified by GC/MS (high resolution) and GC/IR upon comparison with authentic samples. [b] [ketone] = 0.065 M. [c] Very weak EPR signal was observed during the course of the reduction of IVa with LDPA or with $LiAlH_4$ in THF at 23 °C. [d] [ketone] = 0.024 M. [e] [ketone] = 0.025 M, [LDPA] = 0.143 M. [f] Three other products were identified by GC/IR and GC/MS: dimer of mesitylphenyl radical (2.1%), *p*-(*n*-hexyl)phenyl mesityl ketone (6.2%), and its corresponding carbinol (1.9%). See Experimental Section. [g] [ketone] = 0.029 M. [h] [ketone] = 0.0765 M. [i] [ketone] = 0.0127 M. [j] [ketone] = 0.061 M.

differ by $>10^2$ s^{-1}, and if k_H· and k_{fX} are competitive the mole fraction of alcohol formed from the reduction of *m*-bromophenyl mesityl ketone (IVb) should be larger than the fraction formed from the reduction of the para isomer. The product ratio obtained for the reduction $P_N/(P_N+P_D)$ is consistent with the kinetics for reaction given for case 2; see Table III (CH_3CN, 61 °C, 15 h; *p*-Br, $P_N/(P_N+P_D)$ = 0.18; *m-Br*, $P_N/(P_N+P_D)$ = 0.30). The fraction $P_N/(P_N+P_D)$ for the ortho isomer, 0.094, reflects both the expected fast fragmentation rate $k_{fo-Br} \approx 10^5$ sec^{-1} and a sterically hindered hydride transfer, since both processes are, presumably, involved in the reduction.

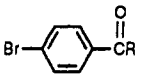
When an efficient hydrogen atom donor, dicyclohexylphosphine (DCPH) was added the ketyl radical could be trapped, and if the alcohol found was the result of both hydride transfer and ET–hydrogen-atom transfer, then the fraction of nondehalogenated alcohol should increase. A comparison of the results of the reduction of IVa with added DCPH is consistent with this competitive pathway, since $P_N/(P_N+P_D)$ = 0.37 while the value obtained from the reduction without added DCPH was 0.18, see Table II.

The reduction of *p*-bromoacetophenone (II) appears to proceed primarily via the hydride transfer pathway, since no dehalogenated products are detected. The analysis of the reduction products of III showed only traces of benzophenone. The reduction of II, III, or IVa with LDPA-d_{24} (solvent acetonitrile) yielded 100% α-D-carbinol, see Table III. Since no dehalogenation was observed from the reactions of II and only a small amount of benzophenone was formed from the reduction of III, carbinol formation could possibly have come from the reaction of the ketyl prior to fragmentation. Carbinols, both halogenated and dehalogenated, are formed during the reduction of IVa. For this substrate, IVa, direct evidence for the formation of a ketyl as a major intermediate is obtained (dehalogenation); however, carbinol formation can also be due to ketyl radical abstraction as well as hydride transfer. The source of hydrogen from either homolytic or heterolytic reduction remained to be established. When the reductions are carried out in THF-d_8 with LDPA or in THF or acetonitrile with LDPA-d_{24}, it is clear that during dehalogenation of IVa the intermediate aryl radical abstracts H or D from LDPA or from solvent; while the source of the carbinol-α-H or -D is entirely from LDPA or LDPA-d_{24}.

In order to elucidate the mechanism responsible for carbonyl reduction, *i.e.*, homolytic or heterolytic hydrogen transfer from LDPA, the reduction of the three halogenated probes (II, III, IVa) was carried out with LAPA-d_{24} in the presence of added DCPH. The reduction of IVa with LDPA-d_{24} with added DCPH confirmed that the transformation of the ketone to carbinol proceeded to a large extent by hydrogen atom abstraction via the ketyl radical ion since the intermediate ketyl is trapped by the hydrogen atom donor, DCPH, see Table III. However, the reductions of either 4-bromobenzophenone or *p*-bromoacetophenone with LDPA-d_{24} in the presence of added DCPH did not show hydrogen incorporation at the α-carbon of carbinol. The formation of carbinol from either *p*-bromobenzophenone or 4'-bromoacetophenone no doubt proceeds by hydride transfer, see Table III. The reduction of the most hindered ketone, 3,3'-dibromo-2,2',4,4',6,6'-hexamethylbenzophenone (V), with LDPA gave only homolytic products, see Table IV. The hydride-transfer pathway appears to be sterically blocked by the interaction of the hindered reducing agent, LDPA, and the hindered ketone probe, V, while the electron-transfer process still proceeds.

The Rearrangement Probe. Since 6-halo-1-hexene had been reported to yield methylcyclopentane during its reduction with LDPA[9] and since LAH gives cyclized

Table III. Deuterium Incorporation during the Reduction of the Aromatic Ketones



R = CH_3, C_6H_5, mesityl

substrate (R)	conditions	products (%) X (%)	Z (%)	SM (%)
CH_3 (III)[a]	THF-d_8/LDPA	Br (100)	H (100)	30.2
	THF/LDPA-d_{24}	Br (100)	D (100)	29.0
	CH_3CN/LDPA-d_{24}, DCPH (0.35 M)	Br (100)	D (100)	4.1
phenyl (III)[b]	THF-d_8/LDPA	Br (100)	H (100)	0.0
	THF/LDPA-d_{24}	Br (100)	D (100)	0.0[c]
	CH_3CN/LDPA-d_{24}, DCPH (0.35 M)	Br (100)	D (100)	0.0[d]

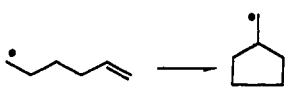
substrate (R)	conditions	products X (%)	yield (%)	X (%)	Z (%)	yield (%)	Z (%)	yield (%)
mesityl (IVa)	THF/LDPA-d_{24}[e]	D (28) H (72)	6.4	D (28) H (72)	D (100)	14.2	D (100)	83.1
	THF-d_8/LDPA[f]	D (6) H (94)	0.67	D (6) H (94)	H (100)	27.3	H (100)	76.4
	CH_3CN/LDPA-d_{24} DCPH (0.35 M)[g]			D (18) H (82)	D (68) H (32)	65.3	D (68) H (32)	36.1

[a,b] [ketone] = 0.010 M, [LDPA] = 0.047 M, 61 °C, 24 h. [c] 0.8% of Ph_2CDOH was detected. [d] 0.76% of Ph_2CDOH was detected. [e] [IVa] = 0.067 M, [LDPA] = 0.177 M, 23 °C, 48 h. [f] [IVa] = 0.067 M, [LDPA] = 0.35 M, 23 °C, 48 h. [g] [IVa] = 0.024, [LDPA] = 0.099 M, 61 °C, 15 h.

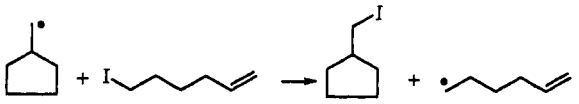
product[15] with 2,2-dimethyl-1-halohexene (x = Br, I) the purified LDPA (LAH free) was allowed to react with 6-halo-1-hexene. The products of these deductions are listed in Table V.

Only minor amounts of methylcyclopentane (4–9%), diagnostic of radical cyclization, are formed during the reaction of 6-iodo-1-hexene (VIa), while no cyclized products are formed during the reaction of 6-bromo-1-hexene (VIb). Only when the reaction is carried out in the presence of a small amount of a radical initiator, AIBN (3%), are traces (0.6%) of the cyclized product produced. The structure of the 3-alkylated pyridine from either substrate only has the uncyclized side chain.

An alternative mechanism for the reductive cyclization of 6-iodo-1-hexene has been suggested.[12h] In this sequence of reactions the cyclized product, 1-methylcyclopentane, can be formed by a chain reaction which does not involve the reagent as a chain carrier, Scheme II. Since reduction



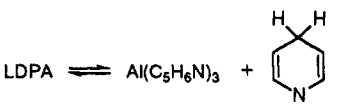
(21)



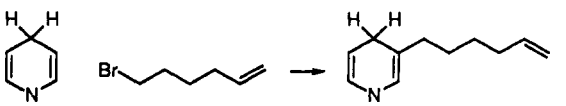
(22)

takes place after the formation of the cyclized iodide, the substrate looses its usefulness as a radical cyclization probe. The minor amount (4–9%) of cyclized hydrocarbon formed in the LDPA reduction, Table V, does not unequivocally confirm the involvement of a radical process. A more diagnostic substrate, 6-bromo-1-hexene, has been used as a cyclization probe, since the halogen-transfer step (*i.e.*, bromine atom transfer), eq 22, does not take place rapidly enough to carry the chain.[12h] A further advantage afforded by the use of the bromohexene is that S_N2 substitution by pyridine or by the pyridyl anion proceeds more slowly than the substitutions with the alkyl iodide.

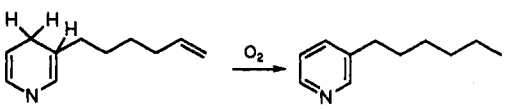
As expected no cyclization was detected when the bromide was reduced by LDPA and no N-substituted pyridinium salt was formed, however, due to the strongly nucleophilic pyridyl anion an almost quantitative yield of the 3-substituted pyridine was formed (eqs 23–25). Only with 3% of added AIBN was a small amount (<1%) of cyclized material detected.



(23)



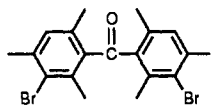
(24)



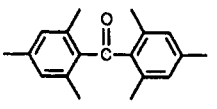
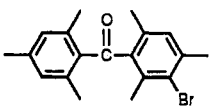
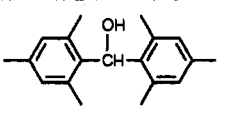
(25)

(15) Walter, M.; Ramaby, L. *Anal. Chem.* **1973**, *45*, 165.

Table IV. Reduction of 3,3'-Dibromo-2,2',4,4',6,6'-hexamethylbenzophenone (V) with LDPA

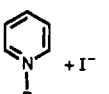


LDPA →

conditions[a]	products, %			SM (%)
				
THF, 23 °C, 24 h	5.9±1.6	24.4±0.8	0.0	68.0±2.3
THF, 61 °C, 22 h	98.9±1.2	0.0	3.3±0.3	0.0

[a] [V] = 0.0046 M, [LDPA] = 0.050 M.

Table V. Reaction of 6-Halo-1-hexene with LDPA (THF)[a]

substrate	conditions	products (%)[b,c]			SM (%)
					
6-iodo-1-hexane	23 °C, 20 h[d]	45.0	8.5	10.5	33.5
	23 °C, 20 h[e]	16.0	4.4	35.7	41.8
	61 °C, 20 h	57.6	9.4	26.4	8.2
6-bromo-1-hexane	61 °C, 36 h	95.9	0	0	4.2
	61 °C, 36 h, 3% AIBN	94.9	0.6	0	4.5

[a] [LDPA]/[RX] = 1.77; [RX] = 0.122 M. [b] R = 5-hexenyl. [c] In all reactions, 3–5% of dihexenylpyridine was detected (GC/MS). [d] [LDPA]/[RX] = 1.77; [RX] = 0.083 M. [e] Nondegassed.

Conclusions. As a reagent LDPA promotes the reduction of ketones and alkyl halides by two competitive pathways: hydride transfer and SET. The dominant pathway for the reduction of both ketones and halides involves a hydride transfer, even though minor amounts of radical derived products or intermediates (*i.e.*, EPR) may be detected. With very good acceptors (*i.e.*, trityl bromide or 2,6-di-*tert*-butylquinone) a SET pathway is dominant. When the ketones that are reduced are sterically hindered and nucleophilic attack by hydride is slowed down, the SET pathway becomes the favored process.

Experimental Section

General. The solutions of all oxygen- and water-sensitive hydride reagents were prepared in a dry box under a N_2 atmosphere. The transfer of the solutions was performed with gas-tight syringes using standard techniques. All the reduction reactions were carried out in flame-dried H tubes which were degassed before they were sealed.

Instrumentation. ^1H and ^2H NMR spectra were obtained using either a Bruker AM-400 (400 MHz) or Bruker WH-200 (200 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 diphenylpicryhydrazyl (DPPH) external standard. IR spectra were recorded on a Perkin-Elmer Model 1600 FT/IR spectrometer. High-resolution mass spectral data were obtained with a KRATOS MS50 high-resolution EI^+ ionization spectrometer (70 eV) connected to a DS 55 data system. The isotopic content of the products was conveniently determined by GC/MS technique in conjunction with ^1H and ^2H NMR. In order to avoid possible error due to partial separation of the isotopic mixtures by GC, the mass fragmentography technique was employed; the total ion mass of each compound (*m/z*) was integrated for each GC peak and used as the numerical value for the analytical calculations. Gas-phase chromatograph–mass spectra (GC/MS) were recorded using 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 using a HP-5965A IRD spectrometer interfaced to a HP5890 gas chromatograph (Hewlett-Packard) 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 distilled from sodium benzophenone ketyl immediately prior to use. THF-d_8 (GIC, 99% D) was purified by the same method. Acetonitrile (Aldrich, reagent grade) was purified by the standard procedure[15] and distilled over CaH_2 before use. *N,N*-Dimethylformamide (DMF, Aldrich, 99%, ACS spectrophotometric grade) was distilled form CaH_2 prior to use.

Lithium aluminum hydride (General Intermediates of Canada) was dissolved in diethyl ether, filtered, and recovered after the ether was evaporated. Lithium aluminum deuteride (Aldrich, 98% atom D) was used as supplied.

LDPA, I, and LDPA-d_{24} (prepared from $LiAlD_4$ and Py-d_5) were prepared at 23 °C.[4,16]

Bromotriphenylmethane (Aldrich, 98%) was recrystallized from benzene/petroleum ether (35–60 °C)[17] mp 153–154.5 °C (lit.[17] 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.[18] mp 103 °C). ***m*-Dinitrobenzene** (Fisher) was recrystallized from methanol, mp 91.5–92 °C (lit.[18] mp 88–90 °C). 1,4-Di-*tert*-butylbenzene (Aldrich), the internal GC standard, was recrystallized from ethanol and dried in vacuum over P_2O_5 at 55 °C, mp 78–79 °C (lit.[18] mp 80 °C).

2,6-Di-*tert*-butylbenzoquinone (Aldrich, >98% purity, mp 65–67 °C) and dicyclohexylphosphine (Aldrich) were used as received.

Benzophenone (Fisher) was recrystallized from petroleum ether (35-60 °C)/acetone, mp 49–50.5 °C (lit.[18] mp 49–51 °C).

Dimesityl ketone (Aldrich) was recrystallized from petroleum ether (35-60 °C)/acetone, mp 139–140.5 °C (lit.[18] mp 138–140 °C).

4-Bromoacetophenone (II) (Aldrich) was recrystallized from ethanol/water, mp 51–52 °C (lit.[18,19] mp 50–52 °C).

4-Bromobenzophenone (III) (Aldrich) was recrystallized from ethanol/petroleum ether (35–60 °C), mp 80.5–81.5 °C (lit.[18,19]

(16) In order to keep the reactions between ketones and LDPA be carried out under the same condition, all the reagent LDPA used in this work was prepared under the same condition.

(17) Fieser and Fieser. *Reag. Org. Synth.* **1967**, *1*, 1254.
(18) Aldrich Catalog Handbook of Fine Chemicals 1990–1991.
(19) *CRC Handbook of Chemistry and Physics*, 62nd ed.; CRC: Boca Raton, FL, 1981.

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.

Mesityl phenyl ketone (2,4,6-trimethylbenzophenone), bromophenyl mesityl ketones (2-, 3-, or 4-bromo-2′,4′,6′-trimethylbenzophenone, IVa-c), and 4-(*n*-hexyl)-2′,4′,6′-trimethylbenzophenone were prepared by treating a CS_2 solution of the corresponding bromobenzoyl chlorides with mesitylene in the presence of aluminum trichloride.[20] The products were isolated and purified by recrystallization from petroleum ether (35-60 °C)/acetone.

Mesityl phenyl ketone: mp 34–35 °C (lit.[20] mp 34–35.5 °C); bp 161–163 °C/4.5 mmHg (lit.[27] bp 180–182 °C/8.5 mmHg); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.78 (m, 2H), 7.60 (m, 1H), 7.46 (m, 2H), 6.94 (s, 2H), 2.37 (s, 3H), 2.08 (s, 6H); HRMS, *m/z*$^+$, 224.1201 (calcd for $C_{16}H_{16}O$ 224.1201); λ_{max} (GC/IR) 3072, 2932, 1815, 1887, 1609, 1450, 1387, 1284, 1173, 1026, 910, 849 cm^{-1}.

4-Bromophenyl mesityl ketone (IVa): mp 71.5–72.5 °C (lit.[20] mp 70–72 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.62 (AB doublet, 4H), 6.92 (d, 2H), 2.34 (s, 3H), 2.06 (s, 6H); HRMS, *m/z*$^+$ 304.0284, 302.0307 (calcd for $C_{16}H_{15}O^{81}Br$ 304.0289; $C_{16}H_{15}O^{79}Br$ 302.0306); λ_{max} (GC/IR) 3019, 2933, 1688, 1587, 1481, 1396, 1263, 1171, 1071, 1013, 907, 847 cm^{-1}. Anal. Calcd for $C_{16}H_{15}OBr$: C, 63.33; H, 5.05; Br, 26.35. Found: C, 63.38; H, 4.99; Br, 26.35.

3-Bromophenyl mesityl ketone (IVb): mp 88–89 °C (lit.[21] mp 87–89 °C); ^{1}H NMR (200 MHz, CD_2Cl_2) δ 7.94 (m, 1H), 7.70 (t-m, 2H), 7.34 (t, 1H), 6.94 (s, 2H), 2.35 (s, 3H), 2.06 (s, 6H); HRMS, *m/z*$^+$, 304.0282, 302.0300 (calcd for $C_{16}H_{15}O^{81}Br$ 304.0289; $C_{16}H_{15}O^{79}Br$ 302.0306). Anal. Calcd for $C_{16}H_{15}OBr$: C, 63.33; H, 5.05; Br, 26.35. Found: C, 63.61; H, 5.10; Br, 26.44.

2-Bromophenyl mesityl ketone (IVc): mp 113–114 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.70 (m, 1H), 7.40–7.30 (m, 3H), 6.90 (s, 2H), 2.33 (s, 3H), 2.12 (s, 9H); HRMS, *m/z*$^+$, 304.0286, 302.0304 (calcd for $C_{16}H_{15}O^{81}Br$ 304.0289; $C_{16}H_{15}O^{79}Br$ 302.0306). Anal. Calcd for $C_{16}H_{15}OBr$: C, 63.33; H, 5.05; Br, 26.35. Found: C, 63.28; H, 4.92; Br, 26.59.

3,3′-Dibromo-2,2′,4,4′,6,6′-hexamethylbenzophenone (V) was prepared by treating a mixture of 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 with a solution of 1.5 mL of bromine (28 mmol) in 10 mL of CCl_4. The bromine solution was added dropwisely while the mixture was stirred at rt. After 1 h, the mixture was heated to reflux for 4 h. The mixture was diluted with ether and washed successfully with aqueous 10% $NaHCO_3$ solution, 5% sodium thiosulfate, and 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, recrystallization from ether/hexane yielded 2.7 g, 52%, of a white solid: mp 103–104 °C. GC (on SE-30) show only one peak. TLC (silica gel, 5/95 diethyl ether/hexane) show only one spot. ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.90 (s, 2H), 2.36 (s, 6H), 2.25 (s, 6H), 2.00 (s, 6H). Anal. Calcd for $C_{19}H_{20}Br_2O$: C, 53.80; H, 4.75. Found: C, 53.73; H, 4.86. HRMS, *m/z*$^+$: 425.9840 (calcd for $C_{19}H_{20}{}^{81}Br_2O$ 425.9840).

6-Bromo-1-hexene (VIb) (Aldrich) was purified by vacuum distillation, bp 68–69 °C/31 mmHg (lit.[18] bp 47–51 °C/16 mmHg).

6-Iodo-1-hexene (VIa) was prepared by treating 6-bromo-1-hexene (Aldrich) with NaI in dry acetone under a nitrogen atmosphere. Fractional distillation gave a colorless liquid: bp 48–49 °C/1.0 mmHg or 86–88 °C/40 mmHg (lit.[9,12b] bp 64–66 °C/12 mmHg); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.89–5.69 (m, 1H), 5.07–4.93 (m, 2H), 3.22–3.15 (t, 2H), 2.14–2.02 (m, 2H), 1.91–1.77 (m, 2H), 1.57–1.42 (m, 2H); HRMS, *m/z*$^+$, obsd 209.9908 (M$^+$, calcd for $C_6H_{11}I$ 209.9906); λ_{max} (GC/IR) 3088, 2999, 2864, 1836, 1643, 1445, 1352, 1288, 1221, 993, 918. Anal. Calcd for $C_6H_{11}I$: C, 34.31; H, 5.28. Found: C, 34.02; H, 5.05.

Dimesitylcarbinol was prepared from the reaction of mesitaldehyde and mesitylmagnesium bromide:[22] mp 150–150.5 °C (lit.[22] mp 149.5–150 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.10 (s, 4H), 6.65 (s, 1H), 2.57 (s, 6H), 2.52 (s, 12H). Anal. Calcd for $C_{19}H_{24}O$: C, 85.03; H, 9.01. Found: C, 85.21; H, 9.07.

Dimesitylmethane was prepared by Baeyer's method:[23] mp 134–135 °C (lit.[23] mp 130–135 °C). Anal. Calcd for $C_{19}H_{24}$: C, 90.42; H, 9.58. Found: C, 90.28; H, 9.44.

2,4,6-Trimethylbenzhydrol and **4-bromo-2′,4′,6-trimethylbenzhydrol** were prepared by the $NaBH_4$ reduction of the corresponding ketones (IVa-c) in 98% ethanol and then recrystallized from diethyl ether/hexane.

2,4,6-Trimethylbenzhydrol: bp 142–144 °C/0.2 mmHg (lit.[26] 154.5–157 °C/0.3 mmHg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (s, 5H), 6.88 (s, 2H), 6.30 (s, 1H), 2.28 (s, 3H), 2.20 (s, 6H). HRMS, *m/z*$^+$, obsd 226.1358 (calcd for $C_{16}H_{18}O$ 226.1358); λ_{max} (GC/IR) 3650, 3027, 2934, 2876, 1945, 1885, 1804, 1724, 1609, 1460, 1453, 1352, 1173, 1014, 846 cm^{-1}. Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.79; H, 7.93.

4-Bromo-2′,4′,6′-trimethylbenzhydrol: bp 165–167 °C/0.01 mmHg; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.42 (A of AB, 2H) 7.12 (B of AB, 2H), 6.85 (s, 2H), 6.25 (s, 1H), 2.28 (s, 3H), 2.23 (s, 6H). HRMS, *m/z*$^+$, obsd 306.0438, 304.0463 (calcd for $C_{16}H_{17}OBr$ 306.0442, 304.0462); λ_{max} (GC/IR) 3651, 2935, 1611, 1488, 1398, 1170, 1073, 1012, 848 cm^{-1}. Anal. Calcd for $C_{16}H_{17}OBr$: C, 62.96; H, 5.61. Found: C, 63.12; H, 5.67.

2-Bromo-2′,4′,6′-trimethylbenzhydrol: mp 109–110 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.46 (d, 1H), 7.35 (d, 1H), 7.17 (t, 1H), 7.06 (t, 1H), 6.75 (s, 2H), 6.17 (s, 1H), 2.17–2.12 (d, 9H); HRMS, *m/z*$^+$, obsd 306.0440, 304.0466 (calcd for $C_{16}H_{17}O^{81}Br$, $C_{16}H_{17}O^{79}Br$; 306.0442, 304.0462); λ_{max} (GC/IR) 3629, 3070, 3016, 2936, 2879, 1921, 1812, 1725, 1610, 1570, 1445, 1386, 1300, 1189, 1133 cm^{-1}. Anal. Calcd for $C_{16}H_{17}OBr$: C, 62.96; H, 5.61. Found: C, 62.91; H, 5.58.

3-Bromo-2′,4′,6′-trimethylbenzhydrol: bp 178–179 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.25 (m, 4H), 6.85 (s, 2H), 6.32 (s, 1H), 2.42 (s, 3H), 2.25 (s, 6H); HRMS, *m/z*$^+$, obsd 306.0439, 304.0465 (calcd for $C_{16}H_{17}O^{79}Br$, $C_{16}H_{17}O^{81}Br$; 306.0442, 304.0462). Anal. Calcd for $C_{16}H_{17}OBr$: C, 62.96; H, 5.61. Found: C, 62.87; H, 5.57.

4-(*n*-Hexyl)-2′,4′,6′-trimethylbenzophenone: bp 153–155 °C/0.02 mmHg (lit.[27] bp 205–210 °C/4 mmHg); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.75 (d, 2H), 7.30 (d, 2H), 6.95 (s, 2H), 2.74 (t, 2H), 2.40 (m, 5H), 2.12 (s, 6H), 1.75–0.85 (m, 11H); HRMS, *m/z*$^+$, obsd 308.2141 (calcd for $C_{22}H_{28}O$ 308.2140); λ_{max} (GC/IR) 2936, 1869, 1683, 1606, 1445, 1387, 1264, 1171, 1018, 909, 848 cm^{-1}. Anal. Calcd for $C_{22}H_{28}O$: C, 85.66; H, 9.15. Found: C, 85.39; H, 9.06.

4-(*n*-Hexyl)-2′,4′,6′-trimethylbenzhydrol: bp 176–178 °C/0.05 mmHg (lit.[27] bp 205–210 °C/4 mmHg); ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.71 (bd, OH), 7.18 (AA′, 4H), 6.88 (s, 2H), 6.32 (s, 1H), 2.64 (t, 2H), 2.32 (s, 3H), 2.28 (s, 6H), 7.00–0.95 (11H); HRMS, *m/z*$^+$, obsd 310.2299 (calcd for $C_{22}H_{30}O$ 310.2297); λ_{max} (GC/IR) 3650, 3021, 2935, 2871, 1721, 1610, 1010, 1509, 1351, 1170, 1015, 848 cm^{-1}. Anal. Calcd for $C_{22}H_{30}O$: C, 85.11; H, 9.74. Found: C, 85.34; H, 9.65.

4,4′-Bis(2,4,6-trimethylbenzoyl)biphenyl [paraDimer of 2′,4′,6′-trimethylbenzophenone]: HRMS, *m/z*$^+$, obsd 446.2241 (calcd for $C_{32}H_{32}O_2$ 446.2246); λ_{max} (GC/IR) 3100–2900, 1685, 1607, 1423, 1281, 1173, 1000, 909, 850 cm^{-1}.

3-(6-Hexenyl)pyridine: bp 88–90 °C/5 mmHg (lit.[28] bp 75–77 °C/2 mmHg); ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.42 (m, 2H), 7.48 (m, 1H), 7.22 (m, 1H), 5.79 (m, 1H), 4.98 (m, 2H), 2.61 (t, 2H), 2.08 (m, 2H), 1.72–1.26 (m, A_2B_2 type, 4H); HRMS, *m/z*$^+$, obsd 161.1204 (M$^+$, Calcd for $C_{11}H_{15}N$ 161.1205); λ_{max} (GC/IR) 3034, 2937, 2867, 1643, 1575, 1424, 1351, 1189, 1125, 993, 915 cm^{-1}. Anal. Calcd for $C_{11}H_{15}N$: C, 81.94; H, 9.38. Found: C, 82.12; H, 9.45.

General Procedure for the Reduction of Substrates with LDPA and the Quantitative GC Analysis of the Products.

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An aliquot of a solution of LDPA or LDPA-d_{24} (0.05–0.25 M) in the desired solvent (THF, CH_3CN, or THF-d_8) was placed in one arm of a Pyrex H tube, and an aliquot of a solution of the substrate (0.02–0.025 M) in the same solvent containing 1,4-di-*tert*-butylbenzene (with or without the additive AIBN, *m*-DNB, or DCPH) 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–V. The reaction tube was cooled and opened, and the reaction was quenched with dilute HCl and dried with anhydrous $MgSO_4$. The reaction mixtures were analyzed by GC.

The product mixtures from the reduction of *p*-bromoacetophenone (II) and 4-bromobenzophenone (III) were 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 bromophenyl mesityl ketones (IVa-c), 3,3′-dibromo-2,2′,4,4′,6,6′-hexamethylbenzophenone (V), 6-halo-1-hexenes (VIa-b), and bromotriphenylmethane 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 were carried out using a HP5840A gas chromotograph 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–V are the average results of two or more independent experiments.

Isotope-Labeling Study. The reductions of substrates (II-IVa) with LDPA-d_{24} in THF or with LDPA in THF-d_8 were carried out as above. The purified products were analyzed by GC, ^{1}H NMR, ^{2}H NMR, and mass spectroscopy to determine the deuterium content of a particular product.

EPR Spectroscopy of the Reaction Mixtures from LDPA or LAH and the Substrates: Bromotriphenylmethane, 2,6-Di-*tert*-butylbenzoquinone, Dimesityl Ketone, Mesityl Phenyl Ketone, and Benzophenone. A THF solution of the substrate (0.02 M) was placed in one of the divided arms of a H tube fitted also with a quartz EPR tube. A second THF solution of LDPA (2.0 mL, 0.02 M) was placed in the second arm of the H tube and the reaction vessel was degassed three times and then sealed. The solutions were mixed at room temperature and the filled EPR tube was immediately placed into the cavity of the EPR spectrometer and their spectra were recorded.

Triphenylmethyl radical[24] and 2,6-di-*tert*-butylbenzoquinone ketyl[10c] radical were observed in a few minutes after the solution of LDPA and the solution of the corresponding substrate were mixed. Their spectra are identical to those reported in the literature.[10c,24]

The mesityl phenyl ketyl radical was obtained after the solution of mesityl phenyl ketone and the solution of LDPA were mixed for an extended period of time (2 d). The EPR spectrum is identical to that appearing in the literature.[9] The same spectrum was obtained when a THF solution of MPK and a THF solution of $LiAlH_4$ were mixed (several minutes).

The dimesityl ketyl radical was observed after the solutions were mixed and allowed to react for an extended period of time (5 d). The spectrum is identical to that in the literature.[9] The same EPR spectrum was obtained when a THF solution of DMK and a THF solution of $LiAlH_4$ were mixed (2 min). After 24 h, the spectrum assigned to the dimesitylmethinyl radical was observed. The EPR spectrum is identical to that appearing in the literature.[13]

No EPR signal was obtained from the reaction of benzophenone with LDPA.

No reaction was observed between dimesitylcarbinol and LDPA. No reaction was observed either between dimesitylmethane and LDPA or between dimesitylmethane and $LiAlH_4$.[25]