A Mechanistic Probe Study of Potential Electron Transfer Reactions of Lithium Dialkylamides

Martin Newcomb,* Michael T. Burchill, and Thomas M. Deeb

Contribution from the Department of Chemistry, Texas A & M University, College Station, Texas 77843. *Received March 7, 1988*

Abstract: *N*-Lithio-*N*-butyl-5-methyl-4-hexenamine (**1**) was employed as a mechanistic probe for electron transfer (ET) reactions with organic oxidants. Oxidation of **1** gave the *N*-butyl-5-methyl-4-hexenaminyl radical (**2**) that cyclized to the 1-methyl-1-(2-*N*-butylpyrrolidinyl)ethyl radical (**3**). Products from radical **2**, formed by decomposition of the corresponding tetrazene in the absence of good trapping agents, were determined. Radical **2** was also produced in radical chain reactions employing an *N*-hydroxypyridine-2-thione carbamate precursor, and the rate constant for cyclization of **2** to **3** was determined by competition between cyclization and trapping of **2** by hydrogen atom donors Bu_3SnH and *t*-BuSH. At 50 °C, the rate constant for cyclization of **2** to **3** is 3.3×10^3 s^{-1} at 50 °C, and an approximate rate constant for ring opening of **3** to **2** at 50 °C is ca. $7-8 \times 10^3$ s^{-1}. Probe **1** reacted with the strong oxidants (*E*)-2-*tert*-butyl-3-phenyloxaziridine (**17**) and thianthrene radical cation perchlorate salt (**20**) by ET; radical **2** thus formed cyclized or reacted further with the oxidants. In a survey study, a variety of weaker oxidants were found not to react with **1** by ET. One-electron oxidation of **1** required an oxidant with a reduction potential > 0.0 V vs NHE; these results permitted an estimation via Marcus theory calculations of the potential for the $R_2N^-/R_2N^\bullet$ couple that is less negative than −0.1 V vs NHE.

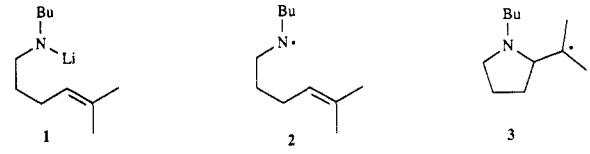
Substantial interest has developed in the possibility that strong bases and nucleophiles can react with weak organic oxidants by an electron transfer (ET) process rather than a conventional two-electron deprotonation, addition, or substitution. While the electron transfer could be either an inner sphere or outer sphere process, it is the outer sphere type that has generally been associated with the term single-electron transfer (SET) reaction (eq 1a). Odd electron products are expected from SET reactions, but such products can also be formed by an inner-sphere process involving addition–homolysis (eq 1b).

$$Nu^- + R \rightarrow Nu^\bullet + R^{\bullet-} \quad (1a)$$

$$Nu^- + R \rightarrow (Nu\text{–}R)^- \rightarrow Nu^\bullet + R^{\bullet-} \quad (1b)$$

The possibility that lithium dialkylamides can react by an ET pathway is intriguing because of the pivotal role of bases such as lithium diisopropylamide (LDA) in synthesis. Over the last decade, several reports of reductions of organic substrates by lithium dialkylamides (mainly LDA) have appeared in which ET from the base to the substrate was either presented as the likely course of the reaction or considered as a potential pathway. The substrates are diverse and include aryl ketones,[1] aliphatic ketones,[2] α-heteroatom-substituted ketones,[3] an anthraquinone,[4] an ynone,[5] thioketones,[6] α-halo imines,[7] a β-thiolactone,[8] an *N*-benzyl carboxamide,[9] α-keto esters,[10] pyridines,[11] alkyl halides,[12] alkyl sulfonates,[13] polycyclic aromatics,[12] an oxaziridine,[14] and molecular oxygen.[15]

In these potential electron transfer reactions, reduced organic substrates have typically been the species detected. However, in an outer-sphere ET reaction of a lithium dialkylamide an aminyl radical must also be formed. Our group has attempted to detect the formation of aminyl radicals by using mechanistic probes, lithium dialkylamides that upon oxidation give aminyl radicals that undergo skeletal rearrangement.[16,17] In this paper we report our studies with the probe *N*-lithio-*N*-butyl-5-methyl-4-hexenamine (**1**).[16] The aminyl radical that would be formed by oxidation of probe **1**, *N*-butyl-5-methyl-4-hexenaminyl (**2**), was found to cyclize to the carbon-centered radical **3**, and an approximate rate constant for the cyclization process has been determined. In reactions with strong oxidants, probe **1** was converted to radical **2** as evidenced by formation of products from radical **3**. However, in reactions of probe **1** with a variety of weak organic oxidants that had been implicated as electron acceptors in reactions with lithium dialkylamides, we found no evidence of formation of radical **2**. Our results show that probe **1** is useful for study of a variety of potential ET reactions and permit a reevaluation of the calculated reduction potential for the $R_2N^-/R_2N^\bullet$ couple.



1 2 3

Preparation of *N*-Butyl-5-methyl-4-hexenamine. Probe **1** was formed by deprotonation of the parent amine, *N*-butyl-5-methyl-4-hexenamine (**4**). Thus, conventional treatment of **4** in

(1) (a) Scott, L. T.; Carlin, K. J.; Schultz, T. H. *Tetrahedron Lett.* **1978**, 4637–4638. (b) Ashby, E. C.; Goel, A. B.; DePriest, R. N. *Tetrahedron Lett.* **1981**, *22*, 4355–4358. (c) Costa, A. M. B. S. R. C. S.; Dean, F. M.; Jones, M. A.; Smith, D. A. *J. Chem. Soc., Chem. Commun.* **1983**, 1098–1099. (d) Koft, E. R.; Smith, A. B., III *J. Am. Chem. Soc.* **1984**, *106*, 2115–2121.

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(17) Newcomb, M.; Williams, W. G. *Tetrahedron Lett.* **1984**, *25*, 2723–2726.

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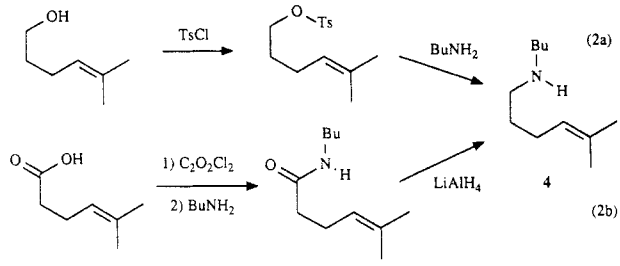
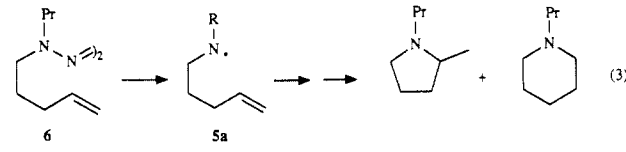
THF at −78 °C with a slight deficiency of *n*-BuLi (hexanes solution) gave **1**. Amine **4** was prepared by two standard routes as described in the Experimental Section. Both amination of the tosylate from 5-methyl-4-hexen-1-ol (eq 2a) and $LiAlH_4$ reduction of the *N*-butyl amide from 5-methyl-4-hexenoic acid (eq 2b) provided amine **4**.



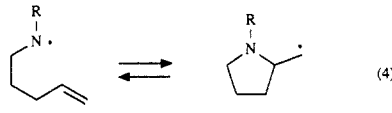
Products from the *N*-Butyl-5-methyl-4-hexenaminyl Radical. For our probe approach to be useful, it is required that aminyl radical **2** cyclizes to give identifiable products. There was ample precedent for the cyclization of the analogous carbon radicals, and the cyclizations of aminium cation radicals containing δ–ϵ unsaturation have been known for quite some time.[18] However, it was not clear at the outset of our study that a neutral aminyl radical with δ–ϵ unsaturation would lead to a substantial amount of cyclized products in the reaction conditions we wished to study.

Michejda et al.[19] reported that *N*-propyl-4-pentenaminyl radical (**5a**), formed by decomposition of the tetrazene **6**, cyclized to give, ultimately, both the product of a 5-exo closure (*N*-propyl-2-methylpyrrolidine) and the product of a 6-endo closure (*N*-propylpiperidine) (eq 3). This result is somewhat unexpected



6 5a

because in kinetically controlled cyclizations of the carbon radical analogues to **5a** the 5-exo product is strongly favored.[18] A further complicating result was obtained by Ingold and Maeda when they[20] attempted to measure the rate constant for cyclization of aminyl radical **5a**. They[20] found that, upon formation of **5a**, no carbon radical could be detected by ESR spectroscopy at low temperature, and they set a small value for the upper limit for the cyclization rate constant ($k < 5\ s^{-1}$ at 25 °C). These two somewhat confusing results might be explained if the cyclization of radical **5a** to radical **7a** is reversible (eq 4); thus, it is possible that Michejda et al.



5a: R = Pr
b: R = Bu

7a: R = Pr
b: R = Bu

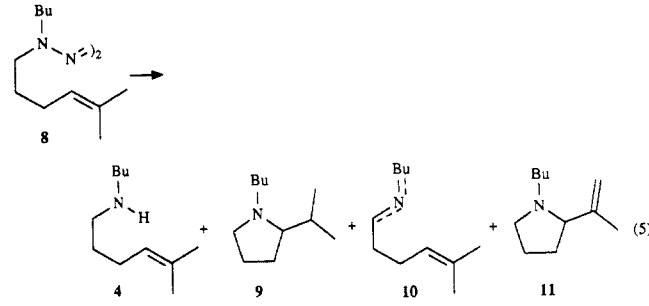
observed products derived from the (at least partially) equilibrated mixture of radicals and that Ingold and Maeda failed to detect carbon radical **7a** because **5a** is favored at equilibrium. In fact, we have found that the *N*-butyl-4-pentenaminyl radical (**5b**) apparently equilibrates with carbon radical **7b** when **5b** is formed in the presence of a poor hydrogen atom donor.[21]

The above results required that we demonstrate that radical **2** could lead to a substantial amount of cyclization products and that we determine what those cyclic products were. Aminyl radical **2** was produced from the symmetrical tetrazene **8** by thermolysis and by photolysis in various solvents in the absence of good radical trapping agents. Under such conditions the radicals should disproportionate, and both reduced and oxidized products from the radicals were expected (eq 5). Table I contains the results of

Table I. Product Yields from Decompositions of Tetrazene **8**[a]

method[b]	temp, °C	solvent	time, h	% yield[c] 4	9	10	11
thermolysis	160	THF	8	30	36	9	3
		c-C_6H_{12}	8	30	33	9	4
photolysis	25	THF	5	31	15	14	18
		ether	5	32	10	18	14
		c-C_6H_{12}	5	32	12	20	16

[a] Average of five runs for thermolysis in THF; average of two runs for other decompositions. [b] Method of initiation. [c] Absolute yields measured against an internal standard.



4 9 10 11

the tetrazene decomposition studies. Both acyclic and cyclic products were detected by GC. Products **4** and **9**, the major products formed by thermolysis of **8** at 160 °C, were identified by GC coelution with the authentic materials and by comparison of the mass spectra of the products with those of the authentic materials. The imines **10** and the oxidized pyrrolidine **11** were identified by analysis of their mass spectra and their GC retention times. No other low-weight products were observed in the tetrazene reactions; the remaining mass balance probably was in the form of high-weight radical coupling products including the hydrazine from coupling of two aminyl radicals, but we did not analyze for high-weight products. An authentic sample of *N*-butyl-2,2-dimethylpiperidine (**12**) was prepared, and we were able to demonstrate conclusively that this 6-endo cyclization product was not formed from radical **2** under our conditions. It is noteworthy that radicals **2** and **3** did not react appreciably with ethereal solvents;[22] since our studies with probe **1** were conducted in THF, the results in Table I show that radicals, if formed from **1** in the studies discussed below, did not react with the solvent.

In order to determine whether or not the oxidized pyrrolidine product **11** was formed in secondary reactions of pyrrolidine **9**, photolyses of tetrazene **8** in cyclohexane were conducted for varying times such that the product distribution could be determined before the tetrazene had reacted completely. At 1-, 2-, and 3-h irradiation times, the ratio of **9**:**11** was constant, which indicated that **11** was a primary product from the radical reactions.

The tetrazene decompositions were conducted in relatively nonreactive conditions as is evidenced by the formation of disproportionation products. However, one cannot expect that, in reactions of the lithium dialkylamide probe **1** with oxidants, any radicals formed would have the opportunity to disproportionate, and, thus, the product distribution obtained from decomposition of tetrazene **8** cannot be used in an attempt to quantitate the amount (if any) of one-electron oxidation of probe **1** in the studies discussed below. The tetrazene results are important because they demonstrate that radical **2** can give, ultimately, some five-membered ring products from a 5-exo cyclization and that six-mem-

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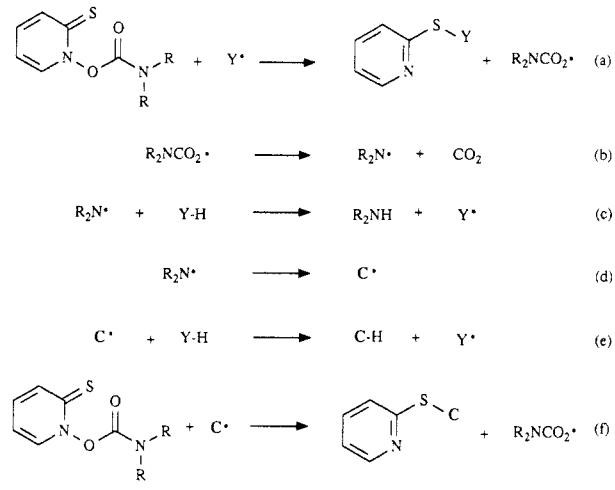
(22) Aminyl radicals are known to react only slowly with hydrogen atom donors; see: Michejda, C. J.; Hoss, W. P. *J. Am. Chem. Soc.* **1970**, *92*, 6298–6301.

Scheme I

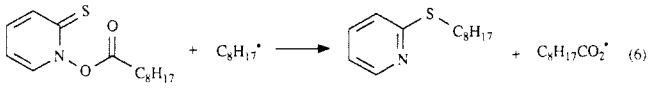


bered ring products are not formed from radical **2**.

Rate of Cyclization of Radical 2. The tetrazene studies demonstrated that cyclization of **2** was possible, but, for a better understanding of the system, we wished to know at least an approximate rate constant for cyclization of **2**. Few rate constants for aminyl radicals have been measured, and we are not aware of reports of any rate constants for cyclization of δ,ϵ-unsaturated aminyl radicals. It was possible that **2** cyclized so slowly that no cyclic products would be formed if **2** was produced in the presence of even a relatively poor radical trapping agent.

In order to determine an approximate rate constant for cyclization of **2**, we employed a competing reactions approach. Aminyl radical **2** was formed in a radical chain reaction from its corresponding *N*-hydroxypyridine-2-thione carbamate (**13**) in the presence of hydrogen atom donors. Radical chain reactions employing *N*-hydroxypyridine-2-thione carbamates and hydrogen atom donors (Y–H) involve the series of reactions shown in Scheme I, steps a–c. Once initiated, the chain sequence is composed of attack of radical Y• on the carbamate to give 2-pyridine-S–Y and a carbamoyloxy radical, decomposition of the carbamoyloxy radical to give CO_2 and an aminyl radical, and reduction of the aminyl radical to give an amine and Y•. When the aminyl radical (R_2N•) can rearrange to a carbon radical (C•) by cyclization, steps d and e of Scheme I (the rearrangement reaction and reduction of the rearranged product by Y–H, respectively) become important. Finally, there is one other possible reaction in the chain sequence for this study; the carbon radical (C•) formed upon cyclization can react with the precursor carbamate to give an alkyl 2-pyridyl sulfide and the carbamoyloxy radical (step f of Scheme I).

From earlier studies, we have available the following information about the competing reaction study. (1) It is known that the aminyl radical does not add to its *N*-hydroxypyridine-2-thione carbamate precursor;[23] thus, there is no nitrogen-centered radical reaction analogous to step f in Scheme I. (2) The rate constant for addition of octyl radical to its *N*-hydroxypyridine-2-thione *ester* precursor (eq 6) is comparable to the rate constant for reaction



of octyl radical with Bu_3SnH.[24] Thus, in a study where a carbon radical is produced from an *N*-hydroxypyridine-2-thione ester in the presence of a large excess of Bu_3SnH, the carbon radical will react virtually exclusively with Bu_3SnH. We assumed at the outset of this study that the reaction of the carbon-centered radical **3** (formed by rearrangement of the aminyl radical **2**) with *N*-hydroxypyridine-2-thione carbamate **13** (step f of Scheme I) would

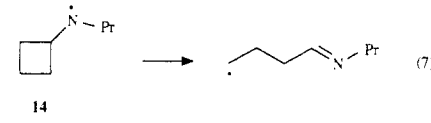
(23) Newcomb, M.; Park, S.-U.; Kaplan, J.; Marquardt, D. J. *Tetrahedron Lett.* **1985**, *26*, 5651–5654.
(24) Newcomb, M.; Kaplan, J. *Tetrahedron Lett.* **1987**, *28*, 1615–1618.

Table II. Products from the Reactions of Aminyl Radical **2** in the Presence of Various Hydrogen Atom Donors at 50 °C in Benzene[a]

H atom donor	concn, M	relative % yield[b]					total % yield[b,c]
		4	**9**	**10**	**11**	**16**	
t-BuSH	0.10	100	<1	0	0	0	90
	0.01[d]	90	10	0	0	0	90
Bu_3SnH	0.11	67	33	0	0	0	90
	0.19	80	20	0	0	0	92
	0.26	84	16	0	0	0	90
	0.50	92	8	0	0	0	110
	1.02	96	4	0	0	0	78
Et_3SiH	0.10	28	14	7	14	37	80
	0.41	40	12	1	14	33	65
	0.50	40	9	1	13	37	64
	1.00	41	12	6	13	28	77

[a] The concentration of precursor **13** varied from 0.008 to 0.010 M. [b] Yields determined by GC. [c] Absolute yields measured against an internal hydrocarbon standard. [d] In this reaction the concentration of the carbamate precursor **13** was 0.0025 M.

have about the same rate constant as the reaction of a carbon radical with the ester analogue of **13** and that step f would not be important when Bu_3SnH or a more reactive hydrogen atom donor was present; the high yields of products **4** and **9** in this work when Bu_3SnH or *t*-BuSH were employed as hydrogen atom donors show that this assumption was reasonable. (3) Finally, approximate rate constants for the reactions of Bu_3SnH and *t*-BuSH with a secondary aminyl radical at 50 °C in benzene are available.[23] These rate constants were determined in another competition study where the competing reaction was the ring opening of the *N*-cyclobutylpropanaminyl radical (**14**), and the values are quite approximate since the rate constant for the reaction in eq 7 is only approximately known.[23]



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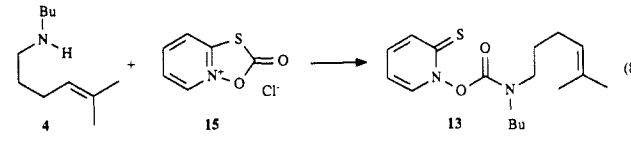
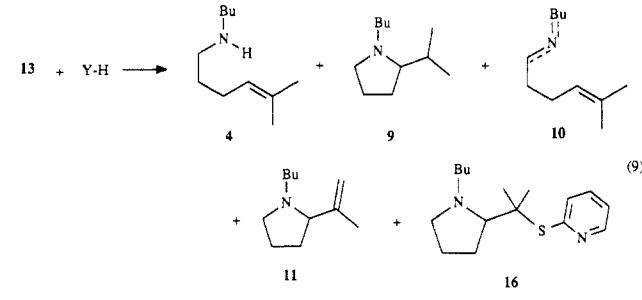
N-Hydroxypyridine-2-thione carbamate **13** was prepared by the standard reaction sequence[21,23] from amine **4** and intermediate **15** (eq 8). Radical chain reactions of carbamate **13** in the



4 **15** **13**

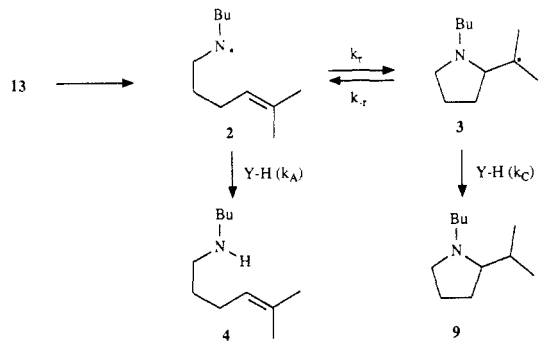
presence of the hydrogen atom donors *t*-BuSH, Bu_3SnH, and Et_3SiH in benzene at 50 °C were initiated by visible light irradiation, and mixtures were analyzed by GC for the products shown in eq 9. The results are collected in Table II. In the presence



4 **9** **10** **11** **16**

of *t*-BuSH and Bu_3SnH, the only low-weight products detected were the acyclic amine **4** and the pyrrolidine **9**. However, with the poor hydrogen atom donor Et_3SiH, radical disproportionation occurred, giving rise to the products from radical oxidation (**10**, **11**) as well as reduction; thus it is clear that in the Et_3SiH studies the velocity of the radical chain processes was slow relative to that of the initiation reaction, and relatively large concentrations of radicals were present. Further, with Et_3SiH as the radical trapping agent, adduct **16** was obtained; this product can arise not only

Scheme II



from the reaction of the carbon-centered radical **3** with the precursor **13** (step f of Scheme I) but also (since the concentration of radicals is known to have been high) from radical–radical coupling between carbon radical **3** and the 2-pyridinethiyl radical.

In a kinetic analysis of the results in Table II, one is interested in the competition between reaction of aminyl radical **2** with the hydrogen atom donor and cyclization of radical **2**. Since the normethyl analogue (**5b**) of radical **2** apparently cyclizes reversibly,[21] one must a priori be concerned about the possible *ring opening* of radical **3**; thus, Scheme II shows all of the reactions of interest when a good hydrogen atom donor is present. The only source of carbon radical **3** is the cyclization of aminyl radical **2**, and a steady state treatment of radical **3** is possible. From such an approach, eq 10 can be derived to give the ratio of acyclic amine

$$\mathbf{4}/\mathbf{9} = k_A k_{-r}/k_C k_r + k_A/k_r \times [\text{Y–H}] \qquad (10)$$

4 to pyrrolidine **9** as a function of the concentration of hydrogen atom donor when that donor concentration is large and unchanging over the course of the reaction. In eq 10, k_A and k_C are the second-order rate constants for reactions of the aminyl and carbon radicals with the hydrogen atom donor, k_r and k_{-r} are the first-order rate constants for the cyclization and opening reactions, respectively, and [Y–H] is the concentration of the hydrogen atom donor.

When the concentration of Y–H is large and virtually unchanging over the course of the reaction, a simple plot of the ratio of products (**4**/**9**) versus the concentration of Y–H will have a slope of k_A/k_r. For the results in Table II with Bu_3SnH as the hydrogen atom source, a plot of **4**/**9** versus [Bu_3SnH] is shown in Figure 1. The least-squares slope was (24.3 ± 0.6) M^{-1} (where the error is 2σ). With use of the crude value of 8×10^4 M^{-1} s^{-1} for the rate constant for reaction of a secondary aminyl radical with Bu_3SnH (k_A) at 50 °C,[23] the rate constant for cyclization of aminyl radical **2** is about 3.3×10^3 s^{-1} at 50 °C.

The intercept of the function in eq 10 contains the ratio k_A/k_r, which is available from the slope of eq 10 and k_C. The value k_C for a typical tertiary radical reacting with Bu_3SnH at 50 °C is 2.3×10^6 M^{-1} s^{-1}.[25] It is apparent that a relatively small value for k_{-r} ($< 1 \times 10^5$ s^{-1}) will give a near-zero intercept for this plot. In practice, the least-squares intercept in Figure 1 was effectively zero (−0.7), which confirms that ring opening of carbon radical **3** is slow relative to trapping of **3** by Bu_3SnH.

Since the ring opening of carbon radical **3** is too slow to be important in the presence of Bu_3SnH, it must also be unimportant in the presence of the better hydrogen atom donor *t*-BuSH.[26] Thus, the rate constant for cyclization of aminyl radical **2** can be calculated for the one experiment involving *t*-BuSH (at 0.01 M) in which cyclic product was detected in an appreciable amount by using eq 11. In eq 11, $[t\text{-BuSH}]_m$ is the mean concentration

$$k_r = \mathbf{9}/\mathbf{4} \times k_A \times [t\text{-BuSH}]_m \qquad (11)$$

of the hydrogen atom trapping agent in this reaction and k_r and k_A are the rate constants for rearrangement of **2** and trapping of

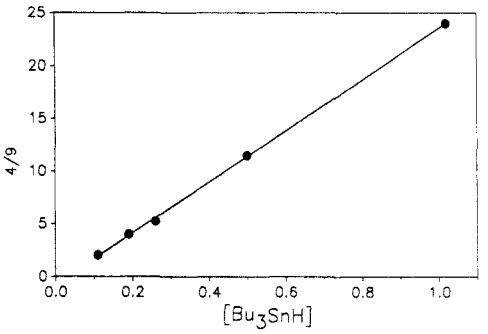


Figure 1. Data from Table II for the trapping and rearrangement of aminyl radical **2** in the presence of Bu_3SnH.

2 by *t*-BuSH, respectively (see Scheme II). With use of a value of $2\text{–}3 \times 10^6$ M^{-1} s^{-1} for trapping of a secondary aminyl radical by *t*-BuSH at 50 °C,[23] the rate constant for cyclization of **2** is $2\text{–}3 \times 10^3$ s^{-1} at 50 °C, a good agreement with the value obtained above in the tin hydride study.

Despite the agreement in the values of k_r determined against the two hydrogen atom donors, one should note that the absolute values for the competing reactions, the reactions of an aminyl radical with the hydrogen atom donors, are only approximately known. Both of the hydrogen atom transfer rate constants are based on the approximate value for the rate constant for opening of the *N*-cyclobutylpropanaminyl radical (**14**), and this value should be considered a minimum.[20] If the basis ring opening reaction of **14** actually has a larger rate constant, then the rate constants for hydrogen atom transfer (k_A) are accordingly larger than the values we used and, consequently, the rate constant for cyclization of aminyl radical **2** is larger than the result we have calculated here.

The data in Table II for the reactions conducted in the presence of Et_3SiH is difficult to analyze because radical populations obviously became high in these runs. Further, the rate constant for reaction of an aminyl radical with Et_3SiH (k_A) is not available. Treatment of the data for the Et_3SiH reactions by the graphical method of eq 10 (using either the ratio of **4**/**9** or the ratio of the sum of all acyclic materials to that of all cyclic materials) gave a small (0.4 or 1.5 M^{-1}) slope, which was expected because the rate constant for reaction of an aminyl radical with Et_3SiH should be small. In addition, a nonzero value was found for the intercept in the graphical treatment which indicates that the radicals **2** and **3** were equilibrating in the time frame of their reactions with Et_3SiH. Since the value of k_A/k_r appears in both the intercept and the slope in eq 10, one can divide out this ratio in a calculation of k_{-r} from the intercept. Using a value of ca. 5×10^3 M^{-1} s^{-1} for the rate constant for reaction of a carbon radical with Et_3SiH (k_C) at 50 °C,[26] we calculated a rate constant for the *ring opening* of **3** to **2** of $k_{-r} = 7\text{–}8 \times 10^3$ s^{-1} at 50 °C. We caution that this can only be considered as a *very* approximate value for ring opening of carbon radical **3**.

Nevertheless, the equilibrium between aminyl radical **2** and carbon radical **3** appears to favor **2** unlike the case for the analogous 5-endo cyclizations of the carbon radical analogs of **2** (e.g. 5-hexenyl radical) where the cyclic radical is strongly favored.[18] It would appear that our conjecture that Ingold and Maeda's inability to detect radical **7a** by ESR spectroscopy[20] resulted from an unfavorable equilibrium between **5a** and **7a** rather than a slow cyclization of **5a** is correct.

The results discussed in this section provided an approximate rate constant for the cyclization of aminyl radical **2**. Inherently, aminyl radicals are of low reactivity in comparison to carbon radicals.[23] Since aminyl radical **2** can cyclize in the presence of good hydrogen atom donors like Bu_3SnH and *t*-BuSH, it should also be likely to cyclize if formed in probe studies by the one-electron oxidation of lithium amide probe **1**.

Reactions of Probe 1 with Strong Oxidizing Agents. Having established that cyclization of aminyl radical **2** occurred and that the rate constant was apparently large enough to permit at least a qualitative probe study with **1**, we can now consider reactions

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(26) Newcomb, M.; Park, S.-U. *J. Am. Chem. Soc.* **1986**, *108*, 4132–4134.

Table III. Products from Reactions of Probe **1** with Strong Oxidizing Agents in THF at 25 °C

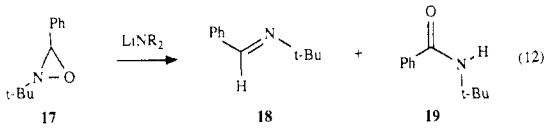
entry	[1][a]	oxidant	concn[b]	% yield[c] 4	9	11	18	cycle/ oxidant[d]
1	0.10	none		100	<0.1			
2	0.05	**17**	0.01	88	2.8		72	0.19
3			0.02	80	4.4		70	0.16
4			0.04	76	8.8		80	0.14
5	0.10		0.02	93	2.7		78	0.17
6			0.04	89	3.8		80	0.12
7			0.08	82	5.7		81	0.09
8	0.07	**20**	0.017	93	0.4	2.6		0.12
9			0.035	84	0.5	5.8		0.13
10[e]			0.07	76	0.7	12		0.13

[a] Initial molar concentration of probe **1**. [b] Initial molar concentration of oxidant. [c] Absolute yield determined against an internal standard. [d] Ratio of moles of cyclic products formed to moles of oxidant employed; see text. [e] Average of four determinations.

of **1** with strong oxidizing agents. Reactions with (*E*)-2-*tert*-butyl-3-phenyloxaziridine (**17**) and thianthrene radical cation perchlorate salt were studied.

Previously, we had found that the normethyl analogue of probe **1**, *N*-lithio-*N*-butyl-4-pentenamine, cyclized slowly on standing at 25 °C presumably via a simple anionic cyclization.[27] Control experiments with probe **1** showed that, in the absence of additives, the lithium amide in THF solution did not cyclize on the time scale of the oxidation experiments we performed (entry 1, Table III).

Newcomb and Reeder reported that oxaziridine **17** reacted with lithium dialkylamides in THF to give, ultimately, imine **18** and amide **19** by two competing reaction pathways (eq 12).[14] Imine



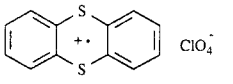
17 18 19

18, the major product in these reactions, was formed slowly in comparison to the loss of oxaziridine **17**, and a relatively stable intermediate species on the pathway from **17** to **18** was indicated.[14] Based primarily on overall reaction velocities and the fact that lithium tetramethylpiperidide (a base with no β-hydrogen atoms) led to large amounts of **18**, they concluded that the reduction of **17** by $LiNR_2$ probably involved an electron transfer reaction.[14] The formation of carbon radicals in reactions of Grignard and lithium reagents with oxaziridine **17**, observed by Davis, indicates that electron transfer processes occur with these nucleophiles.[28] More recently, Rastetter and Wagner concluded that phenolate anions react with an oxaziridine by an initial electron transfer process.[29]

Oxaziridine **17** was treated with an excess of probe **1**. After several hours at 25 °C, the reactions were quenched by addition of water. Under these reaction conditions, oxaziridine **17** was completely consumed.[14] Products were analyzed by GC, and the results are given in Table III (entries 2–7). Pyrrolidine **9** was formed in low yield. Imines **10** from probe **1** were present in the product mixture in low yield, but we could not resolve them from imine **18** by our GC technique, and we could not directly determine the yields of these products. The yield of **18** was calculated as the total amount of oxaziridine **17** used in the study minus the amount of amide **19** formed; in previous work the sum of **18** and **19** accounted for all of the oxaziridine **17** employed.[14]

The last column in Table III gives the ratio of the number of moles of cyclic products formed to the moles of oxidant that reacted by the purported electron transfer reaction. The absolute yield of pyrrolidine **9** in entries 2–7 was found to increase as the ratio of oxidant to probe was increased, but the ratio of cyclized product to oxidant was not constant. The significance of the changing ratio of rearranged product to oxidant is discussed below, but for the objective of evaluating probe **1** as a *qualitative* tool for implicating an electron transfer process, the detection of pyrrolidine **9** is significant. In these reactions free aminyl radical **2** was formed, and, by inference, probe **1** reacted with oxaziridine **17** at least in part by an electron transfer process.

Probe **1** was also allowed to react with the thianthrene radical cation perchlorate salt (**20**). Reactions of Grignard reagents in ether or THF with this salt apparently proceed by electron transfer,[30] and a one electron oxidation of probe **1** was expected.



20

Salt **20** was not noticeably soluble in THF at 25 °C, but dissolution occurred when solutions of probe **1** in THF were added to suspensions of **20** in THF. After standing for several hours, the reaction mixtures were quenched and analyzed by GC. Thianthrene was detected in high yields by GC (84–105%), indicating that the radical cation salt **20** was consumed before the aqueous quench since the radical cation is known to form the corresponding sulfoxide when treated with water.[30] The amine products detected by GC are listed in Table III (entries 8–10).

As with oxaziridine **17**, cyclic products were formed in reactions of probe **1** with salt **20**. However, the major rearranged product was the unsaturated pyrrolidine **11**. We presume that upon cyclization of aminyl radical **2**, carbon radical **3** thus formed was further oxidized by the thianthrene radical cation to give a carbocation. Oxidations of carbon radicals to carbocations have been reported in the reactions of Grignard reagents with **20**.[30] Subsequent reaction of this carbocation with the base present in the reaction mixture could lead to pyrrolidine **11**. If such a sequence operates, then two molecules of thianthrene radical cation and two molecules of base ultimately would be consumed by each electron transfer reaction between **1** and **20**. Of course, other radical reactions would compete with the oxidation of carbon radical **3**.

The ratio of moles of rearranged probe formed to moles of thianthrene radical cation salt used is given in the final column in Table III. If each electron transfer event ultimately consumed two molecules of probe **1** and two molecules of oxidant as we speculate above, then this ratio should be multiplied by two to give the ratio of the molecules of rearranged probe to the number of purported electron transfer events; i.e. about 25% of the maximum amount of rearranged product was formed in each experiment. We presume that this ratio was constant when different amounts of salt **20** were used because, regardless of the amount of thianthrene radical cation salt employed, the reaction occurred at the interface of the solution–solid salt, and, thus, any trapping reaction of radical **2** in competition with cyclization occurred with a pseudo-first-order rate constant. The detection of rearranged products implicates formation of aminyl radical **2** from probe **1**, and an electron transfer from probe **1** to the thianthrene radical cation is strongly suggested.

The oxaziridine and thianthrene radical cation results demonstrate that lithium amide **1** is a successful *qualitative* mechanistic probe that can implicate formation of free aminyl radicals and, by inference, electron transfer processes in reactions with oxidizing agents. However, the availability of *quantitative* information from a study using probe **1** may be questioned. If, in an electron transfer study, one is to employ any probe that can form free radicals, then one must be concerned with the reactions of the free radicals; this applies to radicals formed either by oxidation or reduction processes. Our lithium amide probe **1** is a closed-shell species that has a high intrinsic barrier for outer-sphere electron transfer reactions; for example, the reorganizational

(27) Newcomb, M.; Burchill, M. T. *Tetrahedron Lett.* **1982**, *23*, 4867–4870.
(28) Davis, F. A.; Mancinelli, P. A.; Balasubramanian, K.; Nadir, U. K. *J. Am. Chem. Soc.* **1979**, *101*, 1044–1045.
(29) Wagner, W. R.; Spero, D. M.; Rastetter, W. H. *J. Am. Chem. Soc.* **1984**, *106*, 1476–1480.
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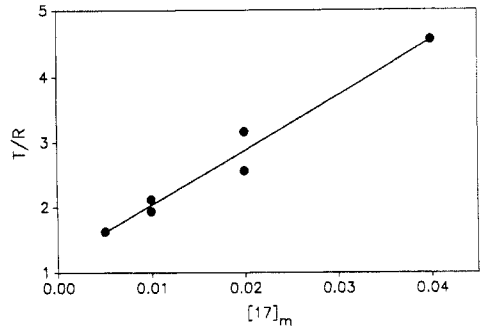


Figure 2. Data from Table III for reactions of probe **1** with oxaziridine **17**. T/R is the ratio of trapped to rearranged radical **2** per mole of oxidant that reacted by ET with **1**. See text for an explanation.

energy (λ) required for electron transfer in the $R_2N^-/R_2N^\bullet$ redox couple has been estimated by Eberson to be ca. 50 kcal/mol (i.e. the activation barrier of the self-exchange reaction is 12.5 kcal/mol).[31] The aminyl radical may have a substantially lower intrinsic barrier to, as well as a more favorable potential for further oxidation.

We speculate that in the thianthrene radical cation studies fast follow-up reactions of aminyl radical **2** with the thianthrene radical cation salt **20**, presumably further oxidation reactions, occurred. This would explain the low and constant amount of rearranged product per mole of oxidant detected in these studies. From this work, the rate constant for cyclization of aminyl radical **2** at 25 °C will be ca. 1×10^3 s^{-1}. Assuming that each electron transfer event led ultimately to consumption of two molecules of oxidant, the ratio of trapped to cyclized aminyl radical was 3:1, and a pseudo-first-order rate constant for trapping of the aminyl radical by solid thianthrene radical cation salt (k_T) is given by eq 13 where k_r is the rate constant for cyclization of **2**. At 25 °C, k_T is approximately 3×10^3 s^{-1}.

$$\text{trapped/rearranged} = k_T/k_r \qquad (13)$$

That the thianthrene radical cation trapped aminyl radical **2** is an educated guess; it is also possible that only a small portion of the probe molecules reacted by an electron transfer process. However, our results with oxaziridine **17** clearly indicate that aminyl radical **2** was trapped by the oxaziridine at a rate competitive with cyclization. Regardless of the overall stoichiometry of the ET reactions, one can plot the ratio of rearranged product to oxidant (last column of entries 2–7 in Table III) against the average concentration of oxidant during the course of the reaction to give a well-correlated function ($r^2 = 0.97$) over the 8-fold concentration range. Further, such a plot will have a slope with a standard deviation of only 10% of the value of the slope.

An example is shown in Figure 2. Here we have assumed that each reaction of **1** with **17** leads ultimately to consumption of 2 mol of oxaziridine. The last column in Table III must be multiplied by two to give the mole ratio of rearranged products per mole of oxidant because only half of the oxidant reacted with probe **1**. Figure 2 is a graphical representation of eq 14 where $[\mathbf{17}]_m$ is the mean concentration of oxaziridine **17** over the course of the reaction. The slope is 84 ± 8 M^{-1} (error is 1σ), and from this

$$\text{trapped/rearranged} = C + (k_T/k_r) \times [\mathbf{17}]_m \qquad (14)$$

slope we can calculate an approximate rate constant for trapping (k_T) by **17** of 8×10^4 M^{-1} s^{-1} at 25 °C (where we have taken k_r at 25 °C to be 1000 s^{-1}). The intercept is 1.2 ± 0.2, showing that at infinite dilution only half of the probe molecules would form cyclic products; since radicals **2** and **3** can equilibrate, this intercept value does not reveal the extent of electron transfer. While the good correlation of eq 14 indicates that oxaziridine **17** trapped aminyl radical **2**, we do not have further information about the nature of this trapping reaction although we would presume that the trapping reaction involves oxidation of intermediates by **17**.

(31) Eberson, L. *Acta Chem. Scand., Ser. B* **1984**, *B38*, 439–459.

Table IV. Reactions of Probe **1** with Organic Oxidants in THF at 25 °C

oxidant	approximate $E°$ [a]	% yield[b] 4	9	10
pyridine	−2.5	100	0	0
p-dicyanobenzene	−2.0	76	0	0
dimesityl ketone	−1.9[c]	92	0	0.1
benzophenone[d]	−1.5	48–59	0	28–44
perylene	−1.4	96	0	2.8
2,4,6-tri-*tert*-butylnitrobenzene	−1.3	92	*e*	0
benzil	−1.1	74	0	17
p-dinitrobenzene	−0.4	51	0	0
$[(Bu_3P)CuI]_4$	−0.1[f]	83	0	0
oxaziridine **17**	>0.0[g]	see Table III		
$[(Bu_3P)AgI]_4$	+0.6[f]	77	5.6	3
thianthrene perchlorate (**20**)	+1.5	see Table III		

[a] $E°$ values taken from ref 36 and 37 unless noted and are adjusted to NHE; the solvents for the electrochemical measurements were acetonitrile or DMF. [b] Absolute yields determined against an internal standard. [c] Based on the value for benzophenone and the report (ref 34) that dimesityl ketone is 0.4 V more difficult to reduce than benzophenone. [d] Several reactions run with 0.1 M probe and 0.1–1 M benzophenone with 0.0 or 0.1 M HMPA. [e] A trace of product (<0.1% yield) with the appropriate retention time for **9** was detected. [f] Based on the value for the perchlorate salt in acetonitrile (ref 38). [g] Reference 35.

Survey of Reactions of Probe 1 with Potential Organic Oxidants. Probe **1** was allowed to react with a variety of oxidizing agents in an attempt to uncover electron transfer processes. The substrates tested were selected either because they are reasonable oxidants or because they have been reported to react with $LiNR_2$ by (outer-sphere) electron transfer. Solutions of **1** in THF were added to suspensions or solutions of the substrates at 25 °C. After 1–2 h, the reactions were quenched, and the products were analyzed by GC. The yields of products from probe **1** are given in Table IV.

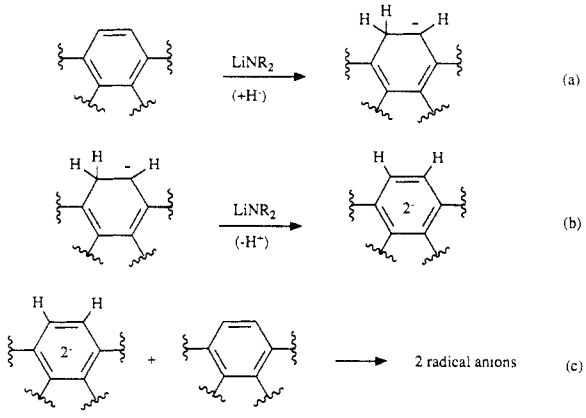
With most of the compounds tested, the starting acyclic amine was returned in high yield, and no cyclic products were detected. A small amount of a compound that had an appropriate retention time for pyrrolidine **9** was observed in the reaction with 2,4,6-tri-*tert*-butylnitrobenzene, but the identity of this component could not be confirmed due to its low yield. Pyrrolidine **9** was formed in the reaction of probe **1** with the THF-soluble silver(I) salt, and this is the only reaction among the survey group that appears to proceed at least in part by outer-sphere electron transfer.

Lithium dialkylamides have been reported to react with benzophenone by electron transfer based on the formation of ketyl or ketyl-derived products.[1a,b] However, Newcomb and Burchill found that, in the reactions of benzophenone with lithium diisopropylamide (LDA) or lithium diethylamide, electron transfer from the base to the ketone did not occur,[32] and benzophenone ketyl was formed in secondary reactions that did not involve $LiNR_2$ as a reducing agent.[33] Dimesityl ketone is more difficult to reduce than benzophenone,[34] and it might be expected to be less likely to react by electron transfer. However, dimesityl ketone should be significantly more persistent in the presence of $LiNR_2$ than benzophenone because the first step in the reaction with $LiNR_2$ with benzophenone is β-hydride transfer from the amide to the carbonyl carbon.[33] A red color indicative of some ketyl formation was observed in our reactions of **1** with dimesityl ketone, but we found no pyrrolidine **9** and thus no evidence of aminyl radical **2** production even upon extended treatment (up to 7 days at 25 °C) of the ketone with **1**.

Several polycyclic aromatic compounds were reported by Ashby's group to react with LDA by electron transfer,[12] and among those perylene has one of the least negative reduction

(32) Newcomb, M.; Burchill, M. T. *J. Am. Chem. Soc.* **1984**, *106*, 2450–2451.
(33) Newcomb, M.; Burchill, M. T. *J. Am. Chem. Soc.* **1984**, *106*, 8276–8282.
(34) Svaan, M.; Parker, V. D. *Acta Chem. Scand., Ser. B* **1982**, *B36*, 365–370.

Scheme III



potentials. We found no evidence for electron transfer from **1** to perylene, and we conclude that $LiNR_2$ does not react with perylene or more difficult to reduce polycyclic aromatics by electron transfer. An alternative pathway for radical formation in reactions of aromatics with $LiNR_2$ can be envisioned (Scheme III). That pathway would involve (a) β-hydride reduction of the aromatic by $LiNR_2$ to give the monoanion of the dihydro aromatic compound, (b) deprotonation of this monoanion by $LiNR_2$ to give a dianion, and (c) electron transfer from the dianion to a neutral molecule to give two radical anions. Scheme III is analogous to the pathway established for ketyl formation in the reaction of benzophenone with $LiNR_2$;[33] while we cannot establish this pathway for reaction of polycyclic aromatics from the data on hand, it accommodates all experimental evidence to date.

Pyridine was reported to react with $LiNR_2$ in THF/HMPA by electron transfer by Newkome's group.[11a] Consistent with the highly negative reduction potential of pyridine, we found no evidence for electron transfer from probe **1** to pyridine. One might predict that the pyridine radical anion could be formed by a hydride addition, deprotonation, redox sequence similar to that in Scheme III. However, such speculation might be premature; we were unable to reproduce Newkome's results with pyridine[11a] even with a variety of experimental modifications.

Probe **1** tested positive for aminyl radical formation (and by inference for outer-sphere electron transfer) in reactions with thianthrene radical cation (E° ca. +1.5 V vs NHE), with $[(Bu_3P)AgI]_4$ (E° estimated at ca. +0.6 V vs NHE) and with oxaziridine **17**. We are unaware of a direct measurement of the reduction potential of **17**, but it must be >0.0 V vs NHE based on the observed strongly positive wave upon reduction of **17** in acidic media.[35] We believe it is reasonable to conclude that outer sphere electron transfer from $LiNR_2$ requires an oxidant with a reduction potential > 0.0 V vs. NHE.

The survey results with probe **1** are consistent with the results our group reported previously for studies with another lithium dialkylamide probe. Newcomb and Williams reported[17] that *N*-lithio-*N*-cyclobutylpropanamine reacted with oxidants **17** and **20** at least in part by ET but that weaker oxidants (pyridine, aryl ketones, iodomethane) did not oxidize the probe in a one-electron transfer reaction.

Reduction Potential for the $R_2N^-/R_2N^\bullet$ Couple. Previously, Eberson concluded from Marcus theory calculations that electron transfer reactions of R_2N^- with trityl chloride and benzophenone were feasible.[31] However, Eberson's calculations were cyclic in a sense since the E° value for the $R_2N^-/R_2N^\bullet$ couple was calculated (again by Marcus theory) to be −(1.1–1.3) V vs NHE based on the presumption[12] that $LiNR_2$ *did* reduce polycyclic aromatics by electron transfer. Our results suggest that the value of E° for the $R_2N^-/R_2N^\bullet$ couple is substantially less negative. For example, using Eberson's model for $R_2N^-/R_2N^\bullet$ where λ_0 = 50 kcal/mol and the very conservative estimates that an acceptor with E° = 0.0 V and a large λ_0 of 50 kcal/mol would react quite rapidly ($k = 1 \times 10^3$ M^{-1} s^{-1} at 25 °C) with R_2N^-, one would calculate an E° for the $R_2N^-/R_2N^\bullet$ couple of only ca. −0.1 V vs NHE, i.e. at least 1 V less negative that Eberson's estimate. Even with what appears to be a generously low value for E° for $R_2N^\bullet$, the one-electron reductions of Ph_3CCl and Ph_2CO by $LiNR_2$ would now be judged to be *not feasible* by Marcus theory with Eberson's criteria[31] (k's of ca. 1×10^{-9} and 1×10^{-14} M^{-1} s^{-1}, respectively).

There is a caveat for use of the calculated E° for the $R_2N^-/R_2N^\bullet$ couple. We have implicitly discussed ET reactions in terms of the outer-sphere mechanism of eq 1a. If the strong oxidants indeed reacted with probe **1** via eq 1a, then our conclusions concerning the feasibility of ET processes for other oxidants will hold for outer-sphere processes, but inner-sphere processes (eq 1b) involving fast bond formation followed by homolysis are still possible ET routes. In fact, it is possible that both oxaziridine **17** and thianthrene radical cation **20** reacted with **1** by inner-sphere routes. For **17** an inner-sphere process is suggested by the accumulation of a detected but unidentified intermediate in reactions of $LiNR_2$ with **17**.[14] Similarly, one can be skeptical about the viability of outer-sphere processes in reactions of **20** with a nucleophile[39a] on the basis of the results of studies of tris(4-bromophenyl)aminium radical cation reactions with nucleophiles.[39] Nevertheless, one should recall that probe **1** tests for aminyl free radicals regardless of the details of the ET process. The results of Table IV show that, for a variety of model oxidants, $LiNR_2$ does not react by either an outer sphere or inner sphere ET process.

Conclusion

N-Lithio-*N*-butyl-5-methyl-4-hexenamine (**1**) can serve as a qualitative mechanistic probe for electron transfer reactions of $LiNR_2$. The radical (**2**) formed upon electron transfer cyclizes somewhat slowly to give a carbon radical (**3**) that is subsequently either reduced or oxidized to give, ultimately, pyrrolidine products. With the approximate rate constant for cyclization of **2** found in this work, one can calculate the approximate rate constants of reactions that trap aminyl radical **2** in competition with the cyclization.

The results of our survey reactions of probe **1** with potential oxidants suggest that $LiNR_2$ is not an especially strong one-electron reducing agent; the oxidation potential previously calculated for this base apparently is substantially in error since it was based on a purported electron transfer process that our results suggest does not occur. Several previous reports that electron transfer occurs between $LiNR_2$ and weak organic oxidants would appear to be in error. Generally those studies were designed around the detection of radical anions (or products derived therefrom) from the organic oxidants, and we would suggest that previously unconsidered secondary reactions like those in Scheme III can account for the formation of radical anion products from the organic oxidant.

Experimental Section

General Procedures. Reactions of air- and water-sensitive reactants were performed in flame-dried glassware flushed with dry argon or nitrogen by using standard techniques. Tetrahydrofuran was dried by distillation from potassium benzophenone immediately before use. Alkyllithium reagents were obtained from Aldrich Chemical Co. as hydrocarbon solutions and were titrated before use. Reagent-grade chemicals were obtained from Aldrich Chemical Co. unless noted and were purified by crystallization or simple distillation. ^1H NMR spectra of $CDCl_3$ solutions were recorded on a Varian EM-390 (90 MHz) or XL-200 (200 MHz) spectrometer; chemical shifts are reported as δ values in ppm relative to internal Me_4Si. ^{13}C NMR spectra of $CDCl_3$ solutions were recorded on a Varian FT-80 (20 MHz) or XL-200 (50 MHz) spectrometer; chemical shifts are reported in ppm relative to internal Me_4Si. IR spectra were recorded on an IBM IR 30/s FT spectrometer.

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(36) Eberson, L. *Electron Transfer Reactions in Organic Chemistry*; Springer-Verlag: Berlin, 1987.

(37) *Encyclopedia of Electrochemistry of the Elements*; Bard, A. J., Lund, H., Eds., Marcel Dekker: New York, 1978, 1979, 1980, 1984; Vol. XII–XIV.

(38) Larson, R. C.; Iwamoto, R. T. *J. Am. Chem. Soc.* **1960**, *82*, 3526–3527.

(39) (a) Eberson, L., private communication. (b) Eberson, L.; Larsson, B. *Acta Chem. Scand., Ser. B* **1986**, *B40*, 210–225; **1987**, *B41*, 367–378.

GC analyses were performed on various instruments with 0.25- and 0.80-mm capillary columns containing nonpolar, bonded phases equivalent to OV-101 or OV-17. GC–mass spectral analyses were performed on a Hewlett-Packard (HP) 5790 chromatograph (0.25-mm capillary column) equipped with an HP 5970 mass selective detector. Temperatures are uncorrected.

***N*-Butyl-5-methyl-4-hexenamine (4)** was prepared from 5-methyl-4-hexen-1-ol (CA registry number 42272-94-6) and from 5-methyl-4-hexenoic acid (CA registry number 5636-65-7).

A. To a stirred solution of 24 g (210 mmol) of 5-methyl-4-hexen-1-ol in 200 mL of dry pyridine at 0 °C was added slowly 54 g (280 mmol) of *p*-toluenesulfonyl chloride. After the addition, the solution was stirred for an additional 0.5 h and allowed to stand at 0 °C overnight. The solution was poured onto 200 g of cracked ice. The tosylate (which separated as an oil) was extracted into ether (3 × 100 mL). The combined ethereal extracts were washed with cold 20% aqueous HCl solution until the pyridine was removed and then with two 100-mL portions of saturated aqueous NaCl solution. The ethereal phase was dried over anhydrous $MgSO_4$. Solvent was removed at reduced pressure to give 45.5 g (170 mmol, 81%) of crude tosylate, which was used without further purification.

The crude tosylate (31 g, 116 mmol) was added dropwise to 350 mL of butanamine. The resulting solution was gently refluxed overnight. Excess amine was removed by distillation, and the resulting salt mixture was made basic by the addition of 10% aqueous NaOH solution. The resulting solution was washed with ether (4 × 100 mL), and the combined ethereal phases were washed with saturated aqueous NaCl solution (2 × 100 mL) and dried with anhydrous $MgSO_4$. Solvent was removed at reduced pressure, and the residual crude amine was distilled to give amine **4** as a clear liquid in 80% yield; bp 69–73 °C (1–3 Torr).

B. To a mixture of 2.33 g (18 mmol) of 5-methyl-4-hexenoic acid in 50 mL of dry benzene with 5 drops of DMF at 0 °C was added dropwise 4.8 mL (7 g, 55 mmol) of oxalyl chloride in 10 mL of dry benzene. The reaction mixture was warmed to room temperature and stirred for 2 h. Excess reagents and solvent were removed by reduced-pressure distillation. The residue was twice treated with benzene (10 mL), and the solvent was distilled. The resulting residue was distilled (bulb-to-bulb), and a fraction was collected at 80 °C (160 Torr). This fraction was dissolved in 10 mL of dry THF, and the resulting solution was added to a solution of 1.66 g (23 mmol) of butanamine and 2.2 g (22 mmol) of triethylamine in 50 mL of dry THF. After being stirred for 1 h, the reaction mixture was treated with 10 mL of water. The layers were separated, and the aqueous layer was extracted with ether (3 × 50 mL). The combined organic extracts were washed with 10% aqueous HCl solution (10 mL), water (10 mL), saturated aqueous $NaHCO_3$ solution (10 mL), and saturated aqueous NaCl solution. The organic layer was dried over $MgSO_4$. Distillation of the solvent at reduced pressure gave crude *N*-butyl-5-methyl-4-hexencarboxamide as a residual oil (1.5 g, 8 mmol, 45%), which was used without purification.

The crude amide (1.5 g) obtained above was dissolved in 10 mL of THF, and the resulting solution was added dropwise to a mixture of 1.22 g of $LiAlH_4$ (32 mmol) in 50 mL of THF. After the addition, the mixture was heated at reflux and monitored by TLC for the disappearance of the amide. When the reduction was complete by TLC, the reaction mixture was treated sequentially with 1.2 mL of water, 1.2 mL of 15% aqueous NaOH solution, and 3.5 mL of water. The mixture was filtered, and the filtrant was washed with dry ether. The combined ethereal solutions were distilled at reduced pressure to remove solvents, and the resulting residue was distilled (bulb-to-bulb) to give 1.0 g (5.9 mmol, 74%) of amine **4** as a colorless oil; bp 80 °C (5 Torr).

Amine **4** had the following NMR spectral properties: ^1H NMR δ 0.9 (m, 3 H), 1.2–1.6 (m, 7 H), 1.55 (s, 3 H), 1.65 (s, 3 H), 2.07 (q, 2 H, J = 10 Hz), 2.55 (t, 4 H, J = 8 Hz), 5.1 (m, 1 H); ^{13}C NMR δ (odd or even number of protons by attached proton test) 14.0 (o), 17.6 (o), 20.5 (e), 25.6 (o), 25.8 (e), 30.2 (e), 32.3 (e), 49.7 (e, 2 C's), 124.7 (o), 131.6 (e).

1,4-Dibutyl-1,4-bis(5-methyl-4-hexenyl)-2-tetrazene (8) was prepared from amine **4** by nitrosation (84%), reduction of the nitrosamine to the hydrazine by $LiAlH_4$ (67%), and oxidative coupling of the hydrazine with red HgO (25% after chromatography). A complete experimental description including ^1H and ^{13}C NMR spectra of the intermediates and of **8** is given in the supplementary material.

1-[[Butyl(5-methyl-4-hexenyl)carbamoyl]oxy]-2(1*H*)-pyridinethione (13) was prepared from amine **4** and 2-oxo-1-oxa-3-thiaindolizinium chloride (**15**)[40] in 72% yield (oil) after chromatography. An experimental description including ^1H and ^{13}C NMR and IR spectral data for **13** is given in the supplementary material.

Decompositions of Tetrazene 8. Stock solutions of **8** in the appropriate solvent (0.08 M) were prepared, and 0.5-mL portions of the stock solution were sealed in Pyrex tubes under vacuum following degassing by three freeze–thaw cycles. Thermolyses were conducted by placing the tubes in a 160 ± 5 °C bath. Photolyses were conducted by irradiating the tubes with a high-pressure, 450-W mercury lamp. After the appropriate time, the samples were removed, and the tubes were cooled in a liquid nitrogen bath and opened. A weighed amount of tetradecane in THF solution was added to the reaction mixtures, and the products were analyzed by GC and GC–mass spectroscopy. Authentic samples of *N*-butyl-2-(1-methylethyl)pyrrolidine (**9**) and *N*-butyl-2,2-dimethylpiperidine (**12**) were prepared for GC and mass spectral comparisons.[41] Imines **10** and *N*-butyl-2-(1-methylidenethyl)pyrrolidine (**11**) were identified by their mass spectral fragmentation patterns.[41] Response factors for **9–11** were assumed to be equal to that of **4**.

Reactions of Carbamate 13. Weighed amounts of **13** and pentadecane (internal standard) were placed in a 10-mL volumetric flask. The vessel was flushed with nitrogen, and degassed benzene was added by syringe to the mark. The resulting stock solution was shielded from light. To 2-mL volumetric flasks were added 1 mL of the stock solution of **13**, the appropriate amount of hydrogen atom donor, and enough degassed benzene to fill the vessel to the mark. The flasks were placed in a constant temperature bath at 50 ± 1 °C. After a 5-min equilibration, the reaction vessels were irradiated with a 100-W, tungsten-filament lamp. The reactions were monitored by TLC for disappearance of **13**. When the reactions were complete, the products were analyzed by GC and GC–mass spectrometry. Products **9–11** were identified as discussed above. Product **16** was identified by mass spectral comparison to an authentic sample.[42] The response factor for **16** was determined on the authentic sample.[42]

Materials for Oxidation Studies of Probe 1. Most of the oxidants were commercially available. (*E*)-2-*tert*-Butyl-3-phenyloxaziridine (**17**) was prepared by the method of Pews.[43] Thianthrene perchlorate (**20**) was a gift from Professor H. J. Shine. Tetrakis(tributylphosphine copper(I) iodide) was prepared by the method of Mann, Wells, and Purdie.[44] Tetrakis(tributylphosphine silver(I) iodide) was prepared by the method of Kauffman and Teter.[45]

Oxidation Studies with Probe 1. Amine **4** in THF was treated with 0.90–0.95 equiv of *n*-BuLi solution in hexane at −78 °C. The resulting mixture was allowed to warm to 0 °C or room temperature. For reactions with oxaziridine **17**, stock solutions of probe **1** containing an internal standard of tetradecane were equilibrated in a water bath at room temperature, and solutions of **17** in THF were added by syringe. For reactions with salt **20**, solid salt **20** was placed in a reaction vessel that was subsequently flushed with nitrogen, and stock solutions of **1** and tetradecane in THF were added. For the survey study in Table IV, stock solutions of **1** (0.1 M) and tetradecane in THF were prepared, and 2 mL of the stock solution was added to a solution or suspension of 0.2–0.4 mmol of the potential oxidant in 3 mL of THF. Reactions were allowed to proceed for 1–2 h at 25 °C. The reactions were treated with water. Products were analyzed by GC after the organic phase was isolated and dried.

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Supplementary Material Available: Experimental details for the syntheses of and spectral data for compounds **8** (and its intermediates) and **13** (3 pages). Ordering information is given on any current masthead page.

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