The weighting scheme used was $w = [\sigma^2(F_o)]^{-1}$. Scattering factors and corrections for anomalous dispersion were taken from a standard source.[24] Corrections for anomalous dispersion were applied to all atoms.

$Au_3Cl_3(\mu\text{-dpma})\cdot CH_2Cl_2$. The positions of the three gold atoms were determined from a sharpened Patterson map. Other atom positions were located from successive difference Fourier maps. Anisotropic thermal parameters were assigned to the elements gold, arsenic, chlorine, and phosphorus. Isotropic thermal parameters were used for all other atoms. All hydrogen atoms were fixed at calculated positions by using a riding model in which the C–H vector was fixed at 0.96 Å, and the isotropic thermal parameter for each hydrogen atom was given a value 20% greater than the carbon atom to which it is bonded. The final stages of refinement included an absorption correcton as described for $Au_2Cl_2(\mu$-dpma). The final R value of 0.051 was computed with a data-to-parameter ratio of 17.6. This yielded a goodness-of-fit of 0.925 and a maximum shift/esd of 0.008 for overall scale on the last cycle of refinement. A value of 2.12 e/Å^3 was found as the largest feature in the final difference Fourier map. This peak was located 1.17 Å from Au(2). The weighting scheme used was $w = [\sigma^2(F_o)]^{-1}$.

$[Au_4Cl_2(\mu\text{-dpma})_2][PF_6]_2\cdot 2CH_2Cl_2\cdot 2H_2O$. The positions of Au(1) and Au(2) were generated from FMAP8. Other atom positions were located from successive difference Fourier maps. The other half of the molecule is generated by inversion. Anisotropic thermal parameters were assigned to the elements gold, arsenic, phosphorus, and chlorine. Anisotropic thermal parameters were also assigned to the phosphorus and fluorine on the anion, each chlorine atom on the dichloromethane solvent molecule, and the oxygen atom on the water molecule. Isotropic thermal parameters were used on all other atoms. The final stages of refinement included an absorption correction and the treatment of all hydrogen atoms as described. The final R value of 0.049 was computed with a data-to-parameter ratio of 14.1. This yielded a goodness-of-fit of 1.040 and a maximum shift/esd of 0.011 for Z/c at C(19) in the last cycle of refinement. A value of 1.79 e/Å^3 was found as the largest feature on the final difference Fourier map. This peak was located 1.15 Å from Au(2). The weighting scheme used was $w = [\sigma^2(F_o)]^{-1}$.

$[Au_4Cl_2(\mu\text{-dpma})_2][NO_3]_2\cdot 4CH_3OH$. The positions of Au(1) and Au(2) were generated from FMAP8. Other atom positions were located from successive difference Fourier maps. Anisotropic thermal parameters were assigned to the elements gold, arsenic, phosphorus, and chlorine. Anisotropic thermal parameters were also assigned to the nitrogen and oxygen on the anion and each oxygen atom on the methanol solvent molecules. Isotropic thermal parameters were used on all other atoms. The final stages of refinement included an absorption correction and treatment of all hydrogen atoms as described for $Au_3Cl_3(\mu$-dpma). The final R value of 0.088 was computed with a data-to-parameter ratio of 16.9. This yielded a goodness-of-fit of 0.937 and a maximum shift/esd of 0.004 for y at C(30) on the last cycle of refinement. A value of 6.34 e/Å^3 was found as the largest feature on the final difference Fourier map. This peak was located 1.15 Å from Au(1).

Acknowledgment. We thank the National Science Foundation (CHE-8519557 and CHE-8941029) for financial support.

Supplementary Material Available: Tables of atomic coordinates, bond distances, bond angles, anisotropic thermal parameters, and hydrogen atom positions for $Au_2Cl_2(\mu\text{-dpma})\cdot 2.5C_6H_5CH_3$, $Au_3Cl_3(\mu\text{-dpma})\cdot CH_2Cl_2$, $[Au_4Cl_2(\mu\text{-dpma})_2][PF_6]_2\cdot 2CH_2Cl_2\cdot 2H_2O$, and $[Au_4Cl_2(\mu\text{-dpma})_2][NO_3]_2\cdot 4CH_3OH$ (18 pages); listings of observed and calculated structure factors (103 pages). Ordering information is given on any current masthead page.

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(24) The method obtains an empirical absorption tensor from an expression relating F_o and F_c. Moezzi, B., Ph.D. Thesis, University of California, Davis, 1987.

(25) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4.

Mechanism of Reduction of Trityl Halides by Lithium Dialkylamide Bases

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Abstract: Trityl chloride (TCl) and bromide are reduced by hindered lithium dialkylamide bases in THF to give predominantly triphenylmethane and a small amount of trityl dimer. Rate constants for the reduction of TCl by lithium diisopropylamide and lithium *tert*-butylethylamide in THF at −78 °C have been measured; the reactions are first order in monomeric base and in trityl chloride. Inter- and intramolecular kinetic isotope effect studies employing β-deuterium substituted bases and substituent effect studies coupled with other kinetic information were used to formulate a scheme for the reactions. The reactions proceed by a rapid predissociation of the trityl halide to form an ion pair containing the trityl–THF oxonium cation followed by diffusion controlled electron transfer (ET) from the monomeric form of the base to the trityl–THF oxonium ion. The radical pair thus formed reacts by fast, highly regioselective β-hydrogen atom transfer from the aminyl radical to the methine carbon of the trityl radical to give triphenylmethane. Radical escape from the cage is a minor competing process. An outer-sphere ET process is energetically acceptable, but an inner-sphere process appears to be more likely.

For several years, our group has been interested in the possibility that hindered lithium dialkylamide bases could react with weak organic oxidants by an electron transfer (ET) process rather than a more conventional heterolytic deprotonation. Several reports appearing since the late 1970s provided evidence that ET reactions from lithium dialkylamides (especially LDA) to a variety of organic substrates might occur.[2] Generally, these studies were product oriented, and, for those that reached mechanistic conclusions, the mechanisms typically were inferred from the detection of radical or radical anion species (or the products derived therefrom) formed from the organic substrate. Our efforts have involved kinetic studies and the application of lithium dialkylamide probes that were designed to signal an ET process by providing upon oxidation aminyl radicals that would rearrange.[3,4] The culmination of the probe work resulted in the observation that electron transfer from $LiNR_2$ was only apparent when the re-

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(1) Department of Chemistry, University of Malaya, 59100 Kuala Lumpur, Malaysia.

(2) For leading references, see: Scott, L. T.; Carlin, K. J.; Schultz, T. H. *Tetrahedron Lett.* **1978**, 4637. Ashby, E. C.; Goel, A. B.; DePriest, R. N. *Ibid.* **1981**, *22*, 4355. De Kimpe, N.; Yao, Z.; Schamp, N. *Ibid.* **1986**, *27*, 1707. Williams, R. M.; Armstrong, R. W.; Dung, J.-S. *J. Am. Chem. Soc.* **1985**, *107*, 3253. Newkome, G. R.; Hager, D. C. *J. Org. Chem.* **1982**, *47*, 599. A more complete list of references is given in ref 3.

(3) Newcomb, M.; Burchill, M. T.; Deeb, T. M. *J. Am. Chem. Soc.* **1988**, *110*, 6528.

(4) Newcomb, M.; Burchill, M. T. *J. Am. Chem. Soc.* **1983**, *105*, 7759. Newcomb, M.; Burchill, M. T. *J. Am. Chem. Soc.* **1984**, *106*, 2450, 8276. Newcomb, M.; Williams, W. G. *Tetrahedron Lett.* **1984**, *25*, 2723.

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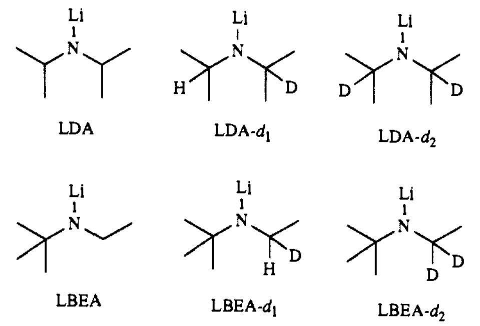


Figure 1. Bases used in kinetic and isotope studies.

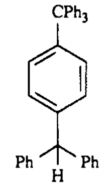
duction potential of the oxidant was greater than ca. 0.0 V vs NHE.[3] From this result, we followed Eberson's application of Marcus theory[5] to calculate a crude reduction potential for the $R_2N^-/R_2N^\bullet$ couple of no less than -0.1 V vs NHE.[3] This value agrees well with those recently reported by Renaud and Fox[6] from cyclic voltammetry of LDA solutions in THF, although the direct electrochemical studies revealed a complex picture with different oxidation potentials for monomeric and dimeric LDA and both temperature and additive effects on the potentials of monomeric LDA.

Throughout our investigations, we have considered the reduction of trityl chloride by $LiNR_2$ bases to be enigmatic. Such reductions are fast and provide triphenylmethane in high yield. Ashby reported that trityl radical was detected by ESR when trityl chloride or bromide was allowed to react with LDA in THF at room temperature and took this as evidence of an ET reaction.[7] However, the ESR signal was reported[7] to grow in long after the trityl halide had been consumed (see below) and obviously had no relevance to the primary reactions. Eberson judged the ET reaction of LDA with trityl chloride to be feasible by Marcus theory calculations,[5] but the estimate of the reduction potential for LDA used by Eberson is now known to be too negative; recalculation of the electron transfer rate constant by Eberson's method[5] with the recently reported values for the LDA potential[3,6] gave a value for the electron transfer rate constant of about 1 × 10^{-9} M^{-1} s^{-1},[3] much too slow to be feasible by Eberson's guidelines.

We now report kinetic, kinetic isotope effect, and labeling studies of the reactions of trityl chloride and bromide with lithium dialkylamide bases in THF. We have found that trityl chloride is reduced to triphenylmethane by β-hydride transfer from the amide base in an associated reaction complex, the formation of which is rate limiting. For LDA and lithium *tert*-butylethylamide (LBEA), the reducing species at -78 °C are the monomeric bases, and the trityl species actually reduced is the trityl-THF oxonium ion formed in equilibrium by dissociation of the trityl halide. The β-hydride transfer process appears to proceed by diffusion-limited ET from the $LiNR_2$ monomer to the oxonium ion to give radicals followed by fast hydrogen atom transfer from the aminyl radical to the trityl radical. Radical escape from the solvent cage competes to a minor extent with the hydrogen atom transfer. The overall reaction sequence is quite similar to the mechanism of homogeneously catalyzed CE (chemical-electrochemical) reductions of highly reactive benzylic halides reported by Merz and Savéant.[8] Our results also offer some insight into the aggregation and reactivity of $LiNR_2$ in THF.

Results

Product Studies. Preliminary studies indicated that reductions of trityl chloride by lithium dialkylamide bases were quite fast, and it was clear that we would be required to attempt kinetic studies at low temperatures. We chose -78 °C as a convenient temperature. When trityl chloride (TCl) was treated with excess LDA or LBEA (see Figure 1) in THF at -78 °C, triphenylmethane (**1**) was the predominant product. A significant minor product was (4-benzhydrylphenyl)triphenylmethane (**2**). It is well-known that **2** is formed from "trityl dimer" **3** in base-catalyzed reactions.[9] Yields of **2** were determined relative to those of **1** by ^1H NMR spectroscopy by comparison of the integrals of the methine protons in each. Another small signal was present in the methine region in some of the ^1H NMR spectra of the product mixtures; we ascribe this signal to the aromatic form of a "trityl trimer". Virtually identical product distributions were found when trityl bromide (TBr) and Ph_3CBF_4 were allowed to react with LDA in THF at -78 °C. Table I lists the product yields.



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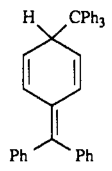

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Table I. Product Yields from Reactions of Trityl Salts with Lithium Dialkylamide Bases in THF at -78 °C

		relative % yield			
substrate	base	**1**	**2**	trimer	total % yield
Ph_3CCl	LDA	91	8	1	99
Ph_3CBr		91	6	3	98
Ph_3CBF_4		92	8		100
Ph_3CCl	LBEA	92	7	1	98

In order to perform isotope labeling and kinetic isotope effect studies, mono- and dideuterated amines were required for the bases in Figure 1. Both of the monodeuterated amines and *N-tert*-butylethylamine-d_2 were prepared by reductions with $LiAlD_4$ of >98% isotopic purity, and all three of these amines appeared to contain the labels at the same level of isotopic purity as judged by ^1H NMR spectroscopy. Diisopropylamine-d_2, however, was prepared by reductive amination of acetone with $NaBD_3CN$ that had been prepared by exchange of deuterium for protium in $NaBH_3CN$. Because we isolated this amine as a dilute ethereal solution, the ^1H NMR spectroscopic analysis was less precise. We can only estimate the deuterium incorporation in this amine to be greater than 95%.

The regiochemistry of the reduction reaction was important both for mechanistic information and for the design of the kinetic isotope effect studies described below. One could anticipate that the sources of hydride were the β-hydrogen atoms of the amide bases, and isopropylideneisopropylamine was detected (but not quantified) by GC analysis of product mixtures from reduction of TCl by LDA. The more important question concerned the position of attack of hydride on trityl. When TCl was reduced at -78 °C with excess LDA-d_2 and with excess LBEA-d_2, ^2H NMR spectroscopic analysis of the purified product triphenylmethane showed that >99% of the deuterium was located at the methine position. This convenient result is only consistent with initial attack of hydride at the methine position of trityl. The deuterated base LBEA-d_2 was of high isotopic purity (see above), and the triphenylmethane formed by reduction with this base contained <2% protium at the methine position as determined by ^1H NMR spectroscopy.

Kinetics Studies. The kinetics of a series of reactions of TCl with LDA and with LBEA in THF at -78 °C were studied. Concentrated base solutions were titrated with a standard solution of menthol in THF and diluted. The reactions were run under pseudo-first-order conditions with at least a 10-fold excess of base. Several mixtures of the reagents were prepared, and periodically a reaction mixture was quenched and assayed for triphenylmethane formation by GC. Pseudo-first-order rate constants for formation

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(5) Eberson, L. *Acta Chem. Scand. B* **1984**, *B38*, 439.

(6) Renaud, P.; Fox, M. A. *J. Am. Chem. Soc.* **1988**, *110*, 5702.

(7) Ashby, E. C.; Goel, A. B.; DePriest, R. N. *J. Org. Chem.* **1981**, *46*, 2429.

(8) Andrieux, C. P.; Merz, A.; Savéant, J.-M.; Tomahogh, R. *J. Am. Chem. Soc.* **1984**, *106*, 1957.

(9) (a) Staab, H. A.; Breitshneider, H.; Brunner, H. *Chem. Ber.* **1970**, *103*, 1101. (b) Guthrie, R. D.; Weisman, G. R. *J. Chem. Soc. D* **1969**, 1316.

Table II. Pseudo-First-Order Rate Constants for Reactions of Trityl Chloride in THF at −78 °C

reagent	concn, M	$10^4k'$,[a] s^{-1}	reagent	concn, M	$10^4k'$,[a] s^{-1}
LDA	0.05	3.6 ± 1.1	LBEA	0.10	6.7 ± 0.4
	0.08	3.2 ± 0.3		0.15	13.6 ± 4.4
	0.10	6.1 ± 1.2		0.20	14.9 ± 1.5
	0.13	5.8 ± 0.9		0.30	19.0 ± 0.3
	0.15	7.4 ± 0.8		0.40	25.2 ± 0.8
	0.20	8.1 ± 1.1		0.50	81 ± 20
	0.30	9.8 ± 0.8	LiN_3	0.006	0.38 ± 0.14
	0.35	10.0 ± 2.0		0.008	0.35 ± 0.09
				0.010	0.20 ± 0.11
				0.012	0.43 ± 0.08

[a] Errors are 1σ.

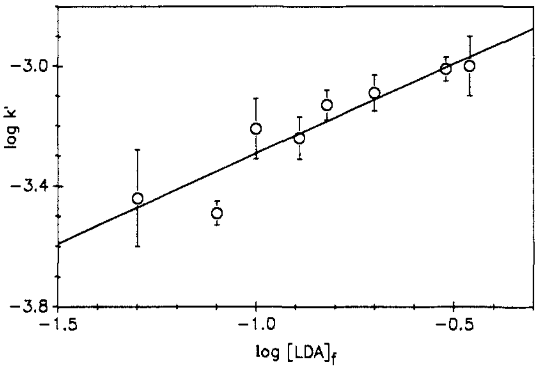

Figure 2. Kinetic results for reduction of trityl chloride by LDA at −78 °C.

of triphenylmethane are given in Table II. These results clearly show that the concentrations of the bases were in the rate laws for the reductions.

The "aliquot" kinetic method with limited sampling gives imprecise results as is clear from the errors listed in Table II. Nevertheless, the LDA data in Table II were readily analyzed. One can express the pseudo-first-order rate constants as a function of LDA concentration as in eq 1 or the equivalent logarithmic form in eq 2 where k' is the pseudo-first-order rate constant, k is the actual rate constant, and p is the kinetic order of LDA. A plot of log k' versus the logarithm of the formal concentration of LDA is shown in Figure 2. The slope of 0.60 shows that LDA is aggregated under our conditions.

$$k' = k[\mathrm{LDA}]^p \tag{1}$$

$$\log k' = \log k + p \log [\mathrm{LDA}] \tag{2}$$

LDA is known to exist as a mixture of monomeric and dimeric forms in THF at low temperatures from freezing point depression studies[10] conducted by Bauer and Seebach at −108 °C and from the electrochemical studies reported by Renaud and Fox[6] at −12 to −78 °C. Using the formal concentrations of LDA in our studies, we solved for the concentrations of monomer and dimer as a function of the equilibrium constant in eq 3 and then solved eq 4 and eq 5 where the subscripts "m" and "d" refer to the monomer and dimer, respectively. When the value chosen for K_{eq} was varied from 1×10^{-5} M^{-1} (effectively all monomer) to 1×10^{6} M^{-1} (effectively all dimer), p_m varied from 0.6 to 1.2 and p_d varied from 0.3 to 0.6. This result is consistent with reaction of LDA as a monomeric species, irrespective of the actual concentrations of monomer and dimer.

$$K_{eq} = [\mathrm{LDA_d}]/[\mathrm{LDA_m}]^2 \tag{3}$$

$$\log k' = \log k_m + p_m \log [\mathrm{LDA_m}] \tag{4}$$

$$\log k' = \log k_d + p_d \log [\mathrm{LDA_d}] \tag{5}$$

The value of K_{eq} was then iterated to give the best solution for $p_m = 1.00$ and $p_d = 0.50$. This solution occurred at $K_{eq} = 22$ M^{-1}. In the freezing point depression studies at −108 °C, Bauer and Seebach[10] found $K_{eq} = 26–27$ M^{-1} for formal concentrations of LDA of 0.17 and 0.08 M. The remarkable agreement between their freezing point depression value for K_{eq} and our kinetic value is better than one might expect from the quality of our data, and we note that the value for K_{eq} for LDA in THF containing 2% HMPA appeared to increase slightly as the temperature was raised.[6] From eq 4 with $K_{eq} = 22$ M^{-1}, log k_m was (−1.9 ± 0.2) where the error is 1σ for the intercept of the function. Thus, k was $(1.4 \pm 0.6) \times 10^{-2}$ M^{-1} s^{-1}. With use of eq 6, where $[\mathrm{LDA}]_f$ is the formal concentration of LDA, and the physically real solution for the quadratic equation described by eq 3, the rate expression for formation of triphenylmethane at −78 °C is given by eq 7 where [TCl] is the concentration of trityl chloride and K_{eq} is equal to 22 M^{-1}.[11]

$$[\mathrm{LDA}]_f = [\mathrm{LDA_m}] + 2[\mathrm{LDA_d}] \tag{6}$$

$$d[\mathrm{Ph_3CH}]/dt = (1.4 \times 10^{-2}\ M^{-1}\ s^{-1})[\mathrm{TCl}](((1 + 8K_{eq}[\mathrm{LDA}]_f)^{0.5} - 1)/4K_{eq}) \tag{7}$$

Reductions of TCl by LBEA in THF at −78 °C were similarly analyzed. Plotting log k' versus the logarithm of the formal concentration of LBEA gave a slope of 1.2 and a value for log k of (−1.9 ± 0.2). It was not possible to obtain a kinetic order of 1.0 for LBEA when all of the kinetic data were used, but, when the imprecise value at 0.5 M LBEA was ignored, the remaining data could be analyzed for a monomer–dimer equilibrium for LBEA by the same procedure as that used above for the LDA data. The value $K_{eq} = 0.5$ M^{-1} gave a kinetic order for monomer of 1.0 and a value for log k of (−2.07 ± 0.12); i.e. k was $(0.9 \pm 0.3) \times 10^{-2}$ M^{-1} s^{-1}. Because the K_{eq} value for LBEA clearly was small, resulting in concentrations of monomer that are close to the formal concentrations of LBEA, and given the error limits for k, the two approaches were judged to be comparable. The rate expression for formation of triphenylmethane at −78 °C in the presence of LBEA is equally well described by eq 8 and by eq 9 where $K_{eq} = 0.5$ M^{-1}.

$$d[\mathrm{Ph_3CH}]/d_t = (1.4 \times 10^{-2}\ M^{-1}\ s^{-1})[\mathrm{TCl}][\mathrm{LBEA}]_f \tag{8}$$

$$d[\mathrm{Ph_3CH}]/dt = (0.9 \times 10^{-2}\ M^{-1}\ s^{-1})[\mathrm{TCl}](((1 + 8K_{eq}[\mathrm{LBEA}]_f)^{0.5} - 1)/4K_{eq}) \tag{9}$$

It may be noted that the assignment of the reactive species in the LBEA reductions as the monomeric form of the base cannot be made a priori. With a kinetic dependence of the reduction near unity, the reactive form of the base could be the dimer (with a large K_{eq}), and the rate constant would simply be twice that given in eq 8. However, the assignment of the monomer as the reactive species for these reductions is supported by the kinetic isotope effect studies discussed below as well as the analogy in the LDA reductions.[13]

Crude kinetic experiments were performed to examine the leaving group effect in the trityl reduction. When trityl bromide

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(10) Bauer, W.; Seebach, D. *Helv. Chim. Acta* **1984**, *67*, 1972.

(11) Aggregation of LDA in THF at low temperatures is indicated by the freezing point depression studies of Bauer and Seebach,[10] the electrochemical studies reported by Renaud and Fox,[6] and the kinetic studies in this work. Recently Galianio-Roth and Collum have questioned the conclusion that substantial amounts of monomeric LDA are present in THF at low temperatures based on NMR studies of isotopically enriched LDA in THF at −106 °C and suggested that impurities may have led to errors in the freezing point depression studies.[12] It would rather appear that the NMR results were misleading.

(12) Galiano-Roth, A. S.; Collum, D. B. *J. Am. Chem. Soc.* **1989**, *111*, 6772.

(13) We recognize the possibility that the kinetic dependence on the concentration of $LiNR_2$ might result from changes in the ionic strength of the medium that affected the ionization rate constant for TCl. Experiments at constant, high ionic strength were considered, but they were deemed to be pointless because we were unable to conceive of an adequate experimental design. The limited solubility of salts in THF at −78 °C is one problem. However, more importantly, changes in solvent ionic strengths should affect the $LiNR_2$ equilibrium constants, and added salts are likely to complex with $LiNR_2$ to give new species. The kinetic effects recently reported for deprotonation of a hydrazone by LDA as the solvent composition was varied amply demonstrate that the base is quite susceptible to subtle medium changes.[12] We consider the similarity in the values for k for LDA and LBEA and the first-order dependence of k_{obs} on $LiNR_2$ monomer concentration to be strong evidence that ionic strength effects on k_{obs} were only small perturbations.

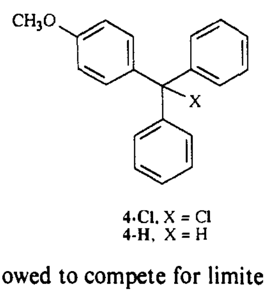
(TBr) was allowed to react with LDA in THF at −78 °C at concentrations comparable to those used in the TCl kinetic runs, triphenylmethane was produced rapidly. The half-life for reaction of TBr was about 0.01 times that of TCl. However, we did not conduct a full kinetic study to determine the order of the base.

Reactions of trityl chloride in THF at −78 °C with other nucleophilic species also were briefly investigated. The reaction of TCl with 3.0 M methanol in THF to give triphenylmethyl methyl ether occurred with an approximate pseudo-first-order rate constant of 7×10^{-8} s^{-1} at −78 °C, several orders of magnitude smaller than the psuedo-first-order rate constants for reactions of TCl with $LiNR_2$.

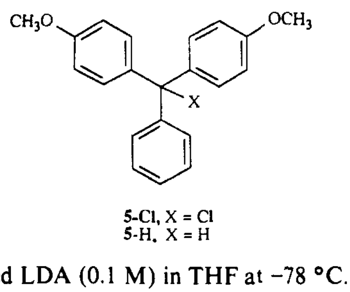
Reactions of TCl with LiN_3 in THF at −78 °C were difficult to perform due to limited solubility of the salt at this temperature. However, solutions of ca. 0.01 M LiN_3 appeared to be homogeneous at −78 °C. TCl was allowed to react with dilute THF solutions of LiN_3 at −78 °C to give trityl azide; the pseudo-first-order rate constants for these reactions are contained in Table II. Due to the large error in these kinetic measurements, the limited range of concentrations of LiN_3 employed, and our lack of knowledge about any aggregation phenomena of LiN_3 under the reaction conditions, we cannot determine the order in LiN_3 for these reactions. If the LiN_3 was not aggregated and the total reaction was a second-order process, first order in azide and in TCl, then the second-order rate constant at −78 °C was ca. 4×10^{-3} M^{-1} s^{-1}.

Kinetic Isotope Effects. A series of kinetic isotope effect studies was conducted at −78 °C. As noted above, TCl reacted with LDA-d_2 and LBEA-d_2 to give triphenylmethane (**1**) that contained deuterium only at the methine position. Therefore, when dideuterated base competed with undeuterated base for limited TCl, the percentage of deuterium at the methine position of product **1** provided a direct measure of k_H/k_D. Reactions of trityl halides with equimolar amounts of dideuterated and undeuterated base were allowed to proceed to completion, and the product **1** was purified by radial chromatography and analyzed by ^{1}H NMR spectroscopy. The percentage of methine protium and the resulting k_H/k_D values are given in Table III. For these intermolecular competition reactions, a small but reproducible value for k_H/k_D of about 1.1 was found. Significantly different results were obtained in intramolecular H–D competition reactions. Both LBEA-d_1 and LDA-d_1 reduced TCl and TBr to give **1** containing 65–70% protium at the methine position (Table III). The resulting k_H/k_D values were about 2.3.

Substrate Competitions. A few competition experiments were performed to gain some understanding of the nature of the reacting trityl species. In one, an equimolar amount of TCl and (4-methoxyphenyl)diphenylchloromethane (**4-Cl**) (0.2 M each) were allowed to compete for limited LDA (0.1 M) in THF at −78 °C. The ratio of the products triphenylmethane (**1**) to (4-methoxyphenyl)diphenylmethane (**4-H**) was 1.7. In a similar experiment, TCl competed with bis(4-methoxyphenyl)phenylchloromethane (**5-Cl**); in this case, the ratio of **1** to the substituted triphenylmethane (**5-H**) formed was 2.0. Control experiments established that both **4-Cl** and **5-Cl** were reduced to the corresponding substituted triphenylmethanes in high yield by excess LDA in THF at −78 °C.



4-Cl, X = Cl
4-H, X = H



5-Cl, X = Cl
5-H, X = H

Discussion

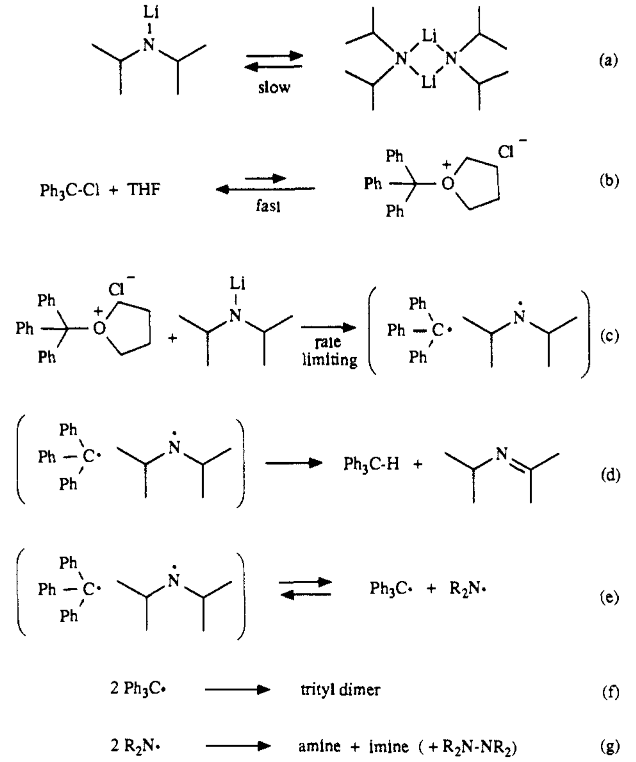
We first address the detection of ESR active species reported by Ashby's group from reactions of TCl and TBr with LDA in THF at room temperature.[7] In these studies, the paramagnetic species were reported to increase in concentration over a 24-h period.[7] From our results, it is apparent that the reactions they were following by ESR spectroscopy did not *involve* TCl or TBr directly. Irrespective of the details of the reaction mechanism, the relatively fast reductions of TCl at −78 °C (half-lives of minutes) require that the reductions at room temperature would be many orders of magnitude faster than the observed rate of formation of ESR active species. The small amount of **2** formed in our reactions shows that some trityl radicals must be formed at −78 °C, and it is possible that, at the beginning of their study, Ashby's group observed a burst of trityl radical from dissociation of "trityl dimer".[14] The slowly increasing ESR signal they observed certainly came from a different source. Triphenylmethane is formed very rapidly in the LDA reactions of TCl and TBr, and it is known that LDA deprotonates triphenylmethane slowly (over several hours) at room temperature.[15] We would speculate that, in the Ashby study, slow deprotonation of triphenylmethane to give trityllithium followed by a reaction of this *anion* (possibly with adventitious oxygen) gave trityl radical. This explanation might be an oversimplification, however, because it is well-known that LDA decomposition in THF[16] would have occurred in the

Table III. Results of Kinetic Isotope Effect Studies[a]

reactant	base	% H[b]	k_H/k_D
Ph_3CCl	LBEA-d_0/LBEA-d_2[c]	53.4	1.15
		51.7	1.07
		53	1.1
Ph_3CBr		51	1.04
		55	1.2
Ph_3CCl	LDA-d_0/LDA-d_2[d]	51	1.1
Ph_3CCl	LBEA-d_1	70	2.3
Ph_3CBr		70	2.3
Ph_3CCl	LDA-d_1	71 (68)	2.4 (2.1)
Ph_3CBr		64 (66)	1.8 (1.9)

[a] Reductions in THF at −78 °C. [b] Percentages of hydrogen determined by ^{1}H NMR spectroscopy; values in parentheses determined by mass spectrometry. [c] The base mixture was 1:1. [d] The base mixture contained 47% of the undeuterated base.

Scheme I



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[14] Jarrett, H. S.; Sloan, G. J. *J. Chem. Phys.* **1954**, *22*, 1783.

[15] Fraser, R. R.; Mansour, T. S. *Tetrahedron Lett.* **1986**, *27*, 331.

[16] Bates, R. B.; Kroposki, L. M.; Potter, D. E. *J. Org. Chem.* **1972**, *37*, 560.

period over which Ashby's group followed the reactions.

A model for trityl halide reduction by $LiNR_2$ is given in Scheme I for reactions of LDA. Despite the complexity, the scheme is consistent not only with the mechanistic requirements of our results but also with a substantial amount of information available in the literature. The isotope effect studies are the most informative, and we consider their ramifications first.

The very similar kinetic isotope effects found in the various reductions suggest quite similar mechanisms for all of the reactions. The small intermolecular kinetic isotope effects observed in the $LiNR_2$-d_0/$LiNR_2$-d_2 competition studies when coupled with the substantially larger intramolecular kinetic isotope effects observed when $LiNR_2$-d_1 was the base require that the reductions occurred with a rate-limiting step that preceded hydrogen atom transfer. For the $LiNR_2$-d_1 reductions, the product distributions were determined in a subsequent hydrogen-transfer process *within a reactive complex* that was subject to a kinetic isotope effect of approximately 2.3.[17]

The results of the kinetic isotope studies also demonstrate that LBEA reacted as a monomer rather than a dimer. The virtual identities in the product compositions from the LDA and LBEA isotope effect studies coupled with the fact that LDA was found to react as a monomer is strong evidence that LBEA also reacted as a monomer, but the results can be analyzed in more detail. If LBEA reacted as a dimer, then the species in a solution containing a 1:1 mixture of LBEA-d_0 and LBEA-d_2 would be 25% LBEA-d_0/LBEA-d_0, 50% LBEA-d_0/LBEA-d_2, and 25% LBEA-d_2/LBEA-d_2. The resulting reduction of TCl would give 25% T–H, 25% T–D, and 50% of a mixture of T–H and T–D. Now, given the model of a reactive LBEA dimer, the kinetic isotope effect expected for the LBEA-d_0/LBEA-d_2 dimer would almost certainly be the same as that observed when the LBEA-d_1 dimer was the base in the *intramolecular* kinetic isotope effect study, i.e. $k_H/k_D = 2.3$. Thus, the composition of products from reduction by the LBEA-d_0/LBEA-d_2 dimer would be 35% T–H and 15% T–D. Summing the various components gives a predicted overall product composition of 60% T–H and 40% T–D; the ratio is far from that observed experimentally. In the "dimer" model, a kinetic isotope effect of 1.2 for the reduction by the isotopically mixed dimer would be required to give an overall observed isotope effect of 1.1, but there is no reason to expect this isotope effect.

The similarity of the kinetic isotope effects observed in the TCl and TBr reductions is also important. This shows that, despite the fact that TBr reacted much faster than TCl, the actual species that were reduced in the two cases were very similar if not the same.

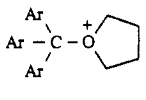
The observed intramolecular isotope effects are consistent with a highly exothermic product-discriminating step. The values are only on the order of 10–15% of the maximum primary isotope effect possible at −78 °C.

The first-order dependence of the TCl reductions on $LiNR_2$ monomer concentration indicates that the stoichiometry in the rate-limiting steps was TCl and $LiNR_2$ monomer. The similar rate constants for reduction of TCl by LDA and LBEA suggest that the steric environment around the base was not especially important in the rate-limiting step. However, with use of the equilibrium constants for dimerization as a guide, LBEA is apparently more hindered than LDA because, in comparison to LBEA, the LDA dimer is more favored with respect to the monomer by about 1.5 kcal/mol. One rationalization for this apparent anomaly would be that an unhindered region of LBEA, the portion involving the ethyl group, approached the trityl species in the rate-limiting step; we consider this unlikely because the rate-limiting step does not involve hydrogen transfer. Rather, it seems more likely that the rate-limiting step was insensitive to steric effects because it involved a diffusion-controlled process. This conclusion is supported by the azide-trapping results as discussed below.

The lithium azide reaction was employed as a test of reactivity because of the well-established fact that azide reacts with trityl[18] and related cations[19] with rates that are nearly at the diffusion-control limit, the so-called "azide clock".[19d] The rate constant we obtained for the reaction of lithium azide with TCl at −78 °C was crude, but it is clear that the $LiNR_2$ reductions of TCl were comparable to if not faster than the rates of azide trapping. Thus, rate-limiting steps involving diffusion-controlled processes are implicated for the $LiNR_2$ reductions.

In order to accommodate the diffusion-controlled rate-limiting step in the context of the small overall rate constants for reduction, it is necessary that TCl itself did not react but rather formed a highly reactive species in a rapid prior equilibrium. The similarity in the kinetic isotope effects for the TCl and TBr reductions and the similar product distributions from TCl, TBr, and Ph_3CBF_4 also suggest such an equilibration that permitted the substrates to form nearly equivalent reactive species. A prior equilibration is also consistent with the general picture for substitution reactions of TCl in nonpolar media like benzene and CCl_4 where it is commonly assumed that molecular TCl equilibrates with its tight ion pair and the ion pair is the species that is captured by nucleophiles.[20]

In basic solvents like THF, TCl dissociation will result in the formation of the oxonium ion **6** (step b in Scheme I),[21] and substituent effects will be manifested as they influence the overall equilibrium constant for the formation of the oxonium ion. Oxonium ions **6** are reasonably well modelled by the corresponding protonated alcohols **7**. Given that methoxy group substitutions in Ar_3CCl and in protonated alcohols **7** result in virtually identical stabilizations of these species relative to the true cations Ar_3C^+,[22] the overall effect of methoxy substitution on the equilibrium in step b of Scheme I is expected to be small.



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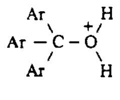

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On the other hand, a large leaving group effect should be observed in THF according to the mechanism of Scheme I. The rate-limiting step involves diffusion-controlled encounter between oxonium ion **6** and the base, and differences between the chloride and bromide ion pairs with the oxonium cation will result in only a very small change in the diffusional coefficients of the complexes. However, the equilibrium constant for dissociation of TBr is substantially larger than that for TCl; quantitative evaluations of the equilibrium constant for dissociation of TBr are not possible because this species reacts too fast.[22] From our results, the equilibrium constant for formation of the oxonium ion from TBr in THF at −78 °C is about 100 times greater than that for TCl. However, given the qualitative nature of the study with TBr, this is only an approximate value.

The rate and equilibrium constants can be considered to test whether or not Scheme I is reasonable. In THF at −78 °C, the diffusion-controlled rate constant (k_D) for uncharged species will be on the order of 3×10^9 M^{-1} s^{-1} based on simple diffusion theory.[23] Attractive ionic forces could result in an accelerated rate constant that might be as great as a factor of ca. 3 for singly

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[17] The small kinetic isotope effect in the intermolecular competition studies results from an increased efficiency of the cage escape reaction for the radical pair containing the dideuterated aminyl radical.

[18] McClelland, R. A.; Banait, N.; Steenken, S. *J. Am. Chem. Soc.* **1986**, *108*, 7023.

[19] (a) McClelland, R. A.; Kanagasabapathy, V. M.; Steenken, S. *J. Am. Chem. Soc.* **1988**, *110*, 6913. (b) McClelland, R. A.; Banait, N.; Steenken, S. *J. Am. Chem. Soc.* **1989**, *111*, 2929. (c) Richard, J. P.; Jencks, W. P. *J. Am. Chem. Soc.* **1982**, *104*, 4689. (d) For a recent example, see: Fishbein, J. C.; McClelland, R. A. *J. Am. Chem. Soc.* **1987**, *109*, 2824.

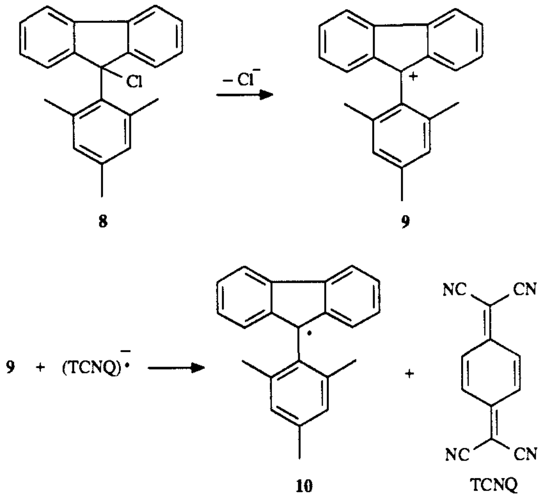
[20] Swain, C. G.; Pegues, E. E. *J. Am. Chem. Soc.* **1958**, *80*, 812. Hudson, R. F.; Saville, B. *J. Chem. Soc.* **1955**, 4130.

[21] (a) Sharp, D. W. A.; Sheppard, N. *J. Chem. Soc.* **1957**, 674. (b) Smith, W. B.; Rao, P. S. *J. Org. Chem.* **1961**, *26*, 254.

[22] Freedman, H. H. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1973; Vol. 4, Chapter 28.

[23] Laidler, K. J. *Chemical Kinetics*, 3rd ed.; Harper & Row: New York, 1987; pp 212–222.

Scheme II



charged ions,[23] so the limit for k_D for THF at −78 °C would be ca. 1×10^{10} M^{-1} s^{-1}. The velocity of the reaction according to Scheme I is given by eq 10. From eqs 10–12, the equilibrium constant for dissociation of TCl in THF at −78 °C (K_{TCl}) is equal to k_{obs}/k_D or about 1×10^{-12} ($\Delta G° = 11$ kcal/mol). This value does not appear to be unreasonable given that the dissociation constant for TCl in nitromethane[24] at 25 °C is about 3×10^{-4} and that nitromethane is about 10 orders of magnitude more basic than THF.[25] An estimate of the dissociation constant for TCl in diethyl ether results by combining K_{TCl} in nitromethane (3×10^{-4}) with the *formation* constant for the trityl–diethyl ether oxonium ion in nitromethane ($K \approx 1 \times 10^{-4}$)[21a] for an estimated K_{TCl} in diethyl ether of about 3×10^{-8} at 25 °C ($\Delta G° = 10$ kcal/mol).

$$d[P]/dt = k_D[LDA_m][\mathbf{6}] \qquad (10)$$

$$d[P]/dt = k_{obs}[LDA_m][TCl] \qquad (11)$$

$$K_{TCl} = [\mathbf{6}]/[TCl] = k_{obs}/k_D \qquad (12)$$

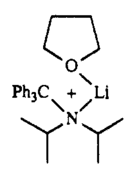
In order to establish a fast equilibrium between TCl and oxonium ion **6**, recombination to give TCl must compete with the diffusion-controlled reaction with of **6** with LDA. At the very low concentrations of **6** formed, this requires that oxonium ion **6** remains associated with chloride anion in an ion pair.

A kinetic requirement of Scheme I is fast radical–radical reactions, the hydrogen atom transfer steps, occurring in competition with diffusion of the radical pair from the solvent cage. Simple radicals couple and disproportionate with one another at the diffusion-controlled rate limit,[26] and the hindered trityl radical also appears to react with small radicals at or near the diffusion limit.[27] The highly regioselective nature of the radical redox reaction, with β-hydrogen transfer from the aminyl radical only to the methine carbon of the trityl radical, is somewhat surprising but consistent with the observation that coupling of the small methyl radical with trityl radical gives only 1,1,1-triphenylethane.[27b]

As noted in the introduction, the mechanism in Scheme I is quite similar to that found by Merz and Savéant[8] in homogeneously catalyzed CE reductions of reactive benzylic halides; Scheme II shows an example. The two chlorides studied in that work, 9-chloro-9-mesitylfluorene and 9-chloro-9-[α-(9-fluorenylidene)benzyl]fluorene, are similar to TCl, and a mechanism involving predissociation of the halides followed by ET was found for several outer-sphere donors with $E°$ from 0.11 to 0.54 V vs SCE. An important difference between those reactions and the reductions of trityl halides studied here is the difference in kinetic control. In our case, the trityl halides and oxonium ion **6** are in equilibrium, and reduction is controlled by the rate of the ET step. For most of the reactions studied by Merz and Savéant, halide dissociation was rate limiting; however, the ET step did become partially rate limiting when excess chloride ion was present and for the donors at the more positive end of the $E°$ scale.[8] It is likely that the change in kinetic control between the two studies resulted mainly from the solvents employed with ion pairing being more important in THF used in this work than in acetonitrile used by Merz and Savéant.[28]

The predissociation mechanism for reductions of halides that can easily form carbocations is readily accommodated by Marcus theory calculations. As noted in the introduction, the calculated rate constant for direct reduction of TCl by LDA is much too small to be feasible. However, the dissociation step provides a strongly oxidizing cation, in this case oxonium ion **6**. Simple Marcus theory calculations suggest that ET from LDA to this species could occur with nearly a diffusion-controlled rate.[29]

The fact that $LiNR_2$ monomer is the active reducing agent in these studies apparently requires that the reduction occurs by an associated complex, i.e. an inner-sphere ET process. This follows from the fact that the LDA dimer is actually a better outer-sphere donor than the monomer as determined in CV studies.[6] One can envision as the reactive intermediate an associated complex such as **11** that can be formed from monomer $LiNR_2$ but not from the dimer. Previously, Renaud and Fox suggested that aggregation of LDA might be quite important in determining the course of a reaction with dimeric LDA leading to ET reaction where the more weakly reducing monomer does not.[6] Our results suggest that the interplay between aggregation and reduction potentials is more complex; the dimer may be a stronger outer-sphere donor but nevertheless a less reactive ET agent due to its inability to form a reactive inner-sphere complex.



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Given that the reductions appear to proceed through an associated complex, the details of the ET process are still not completely clear. In Scheme I, we have shown formation of a caged radical pair by ET and subsequent reaction of the radicals in competition with diffusion, but one cannot rigorously exclude the possibility that H-atom transfer is coupled to ET (i.e. direct hydride transfer). If coupled ET and H-atom transfer does occur, then the associated complex must react by two distinct ET processes (coupled and uncoupled with H-atom transfer) to accommodate the formation of trityl dimer.[32]

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(24) Pocker, Y. *J. Chem. Soc.* **1958**, 240. Evans, A. G.; Jones, J. A. G.; Osborne, G. O. *Trans. Faraday Soc.* **1954**, *50*, 16, 470.

(25) Arnett, E. M.; Progr. *Phys. Org. Chem.* **1963**, *1*, 324.

(26) Fischer, H.; Paul, H. *Acc. Chem. Res.* **1987**, *20*, 200.

(27) (a) Lorand, J. P.; Bartlett, P. D. *J. Am. Chem. Soc.* **1966**, *88*, 3294. (b) Fu, J.-J. L.; Bentrude, W. G. *J. Am. Chem. Soc.* **1972**, *94*, 7710. (c) Huszthy, P.; Lempert, K.; Simig, G.; Tamás, J.; Hegedüs-Vajda, J.; Tóth, G. *J. Chem. Soc., Perkin Trans. II* **1985**, 491. (d) Lorand, J. P.; Wallace, R. W. *J. Am. Chem. Soc.* **1974**, *96*, 1402.

(28) We are indebted to Prof. Savéant for an especially insightful discourse on these points.

(29) The potential for trityl cation in THF is not known, but it is most likely at least as positive as that of trityl cation in DMSO (actually a complex of trityl with DMSO) which has $E_{1/2} \approx 0.2$ V vs SCE at 25 °C.[30] From Renaud and Fox's CV studies, LDA monomer in THF has $E_{1/2} \approx -0.45$ V vs SCE at 25 °C.[6] Thus, $\Delta E°$ is ca. 0.65 V (15 kcal/mol). The self-exchange value (λ_0) for $Ph_3C^+/Ph_3C^\bullet$ is ca. 16 kcal/mol,[31b] and Eberson has estimated the λ_0 value for anionic species like LDA to be 50 kcal/mol.[5] With the approximation that λ for the reaction is the average of the self-exchange values,[5,31a] the rate constant for ET is calculated[5,31a] to be ca. 1×10^{10} M^{-1} s^{-1} at 25 °C. This calculation for outer-sphere ET ignores an ionic work term that should further reduce the barrier to ET; inner-sphere ET would be even more favorable.[31]

(30) Wasielewski, M. R.; Breslow, R. *J. Am. Chem. Soc.* **1976**, *98*, 4222.

(31) (a) Eberson, L. *Electron Transfer Reactions in Organic Chemistry*; Springer: Berlin, 1987; (b) p 51.

Conclusion

The reduction of trityl halides by $LiNR_2$ in THF has been shown to occur by a predissociation mechanism that provides a highly reactive trityl oxonium ion that is subject to reaction with $LiNR_2$ monomer by ET. The mechanism, which bears a striking resemblance to a classical S_N1 reaction, is similar to that previously found for reactions of other easily ionized halides with known outer-sphere ET reductants.[8] The novel aspect is that $LiNR_2$ monomer is not an obvious ET reagent especially in light of the fact that the dimer is a stronger outer-sphere reductant.[6] Reactions of trityl halides with other poor reducing agents such as oxygen bases are also known to give trityl radicals as well as substitution products,[35] and it is possible that these reactions also occur by predissociation of the trityl halides to give a cation followed by ET and coupling reactions. In fact, the predissociation mechanism should be considered the most likely pathway for reactions of triarylmethyl halides with weak electron donors; concerted ET and halogen bond breaking requires a powerful reducing agent.[28,34,36]

Experimental Section

General Procedures. Oxygen- and water-sensitive reactions were performed under nitrogen with flame dried glassware fitted with septa. Solution transfers were performed with gas tight syringes with standard techniques. Reagents were purchased from Aldrich Chemical Co. and were used as received unless otherwise noted. Tetrahydrofuran (THF) was distilled from potassium benzophenone ketyl under N_2 before use. *n*-Butyllithium (in hexanes) was titrated before use.[38] Amines were distilled from CaH_2 under N_2 and stored over KOH. Triphenylmethyl chloride, triphenylmethyl bromide, and triphenylmethane were recrystallized prior to use. Lithium azide was purchased from Eastman Kodak Co. NMR samples were prepared with $CDCl_3$ or acetone-d_6 as solvent and contained ca. 0.1% Me_4Si as an internal reference. ^1H NMR spectra were recorded at 200 MHz and ^{13}C NMR spectra were recorded at 50 MHz with a Varian XL-200 or a Varian Gemini-200 spectrometer. ^2H NMR spectra were recorded at 30 MHz on a Varian XL-200 spectrometer; THF was used as solvent, and chemical shifts were recorded relative to the upfield THF signal defined as 1.73 ppm. GC analyses were performed on a Varian 3400 gas chromatograph equipped with a J&W Scientific megabore column (15 m, DB-1) and a flame-ionization detector; signal integration was achieved with a Varian 4290 integrator. GC–mass spectral analyses were achieved on a Hewlett Packard 5790 GC, which was interfaced to a Hewlett Packard 5970A mass selective detector. Radial chromatography was performed on a Chromatotron Model 7294T chromatograph (Harrison Research Corp). Melting points were determined on a Thomas Hoover capillary melting point apparatus and are uncorrected.

***N*-Ethyl-2-methyl-2-propanamine (*tert*-Butylethylamine).** To 36.5 g (0.5 mol) of *tert*-butylamine was added slowly 50 mL of acetic acid at 0 °C. The mixture was warmed to room temperature, and 47 mL (0.5 mol) of acetic anhydride was added. After being stirred for 3 h, the mixture was heated at reflux for 1 h. After distillation of acetic acid (<140 °C), a solid formed which was recrystallized from ether to yield 23.1 g (40%) of *N-tert*-butylacetamide: mp 101 °C; ^1H NMR δ 1.32 (s, 9 H), 1.8 (s, 3 H), 5.3 (br s, 1 H).

The acetamide (12 g, 0.10 mol) was slowly added to 7.0 g (0.18 mol) of $LiAlH_4$ in 100 mL of anhydrous ether. The mixture was heated at reflux for 24 h. An additional 100 mL of ether was added, and the reaction mixture was heated at reflux for an additional 36 h. Water (5 mL) was added, and the mixture was heated at reflux for 4 h. The volatiles were transferred under vacuum. Distillation yielded 4.1 g (40%) of the *tert*-butylethylamine: bp 86–88 °C; ^1H NMR δ 1.09 (t, 3 H), 1.11 (s, 9 H), 2.59 (q, 2 H); ^{13}C NMR δ 16.11, 29.03, 36.57, 50.21.

***N*-(1-Deuterioethyl)-2-methyl-2-propanamine (*tert*-Butylethylamine-*d*$_1$).** Acetaldehyde (8.8 g, 0.2 mol) was added dropwise to a mixture of *tert*-butylamine (17.5 g, 0.24 mol) and anhydrous potassium carbonate (10 g) at −10 °C. The mixture was stirred for 1 h. The solution was dried with 10 g of 3A molecular sieves. Distillation gave 4.3 g (22%) of *N-tert*-butylacetaldimine: bp 76–78 °C; ^1H NMR δ 1.17 (s, 9 H), 1.96 (d, 3 H, J = 4.8 Hz), 7.69 (q, 1 H, J = 4.8 Hz).

The imine (4.3 g 43 mmol) was added to a mixture containing 0.9 g (21 mmol) of $LiAlD_4$ and anhydrous ether (100 mL). The mixture was heated at reflux for 24 h. Two additional portions of $LiAlD_4$ (0.9 g each) were added during a subsequent 24-h period. Water (3 mL) was slowly added, and the reaction mixture was heated at reflux for 2 h. The product and solvent were vacuum transferred to a −78 °C trap. After drying over potassium carbonate, ether was distilled through a 1 ft Vigreaux column. The residue was dried with CaH_2 and distilled to yield 2.89 g (64%) of product: bp 84–86 °C; ^1H NMR δ 1.09 (d, 3 H), 1.11 (s, 9 H), 2.59 (q, 1 H); mass spectrum, m/e rel abundance) 102 (6, M^+), 87 (100), 58 (70), 42 (25).

***N*-(1,1-Dideuterioethyl)-2-methyl-2-propanamine (*tert*-butylethylamine-*d*$_2$)** was prepared in 40% yield by the method described above for the undeuterated amine but with $LiAlD_4$: ^1H NMR δ 1.09 (s, 3 H), 1.11 (s, 9 H); mass spectrum, 103 (2, M^+), 88 (100), 58 (50), 42 (25).

***N*-(1-Methylethyl)-2-deuterio-2-propanamine (Diisopropylamine-*d*$_1$).** To a stirred mixture of isopropylamine (11.2 mL, 0.19 mol) and 5 g of potassium carbonate at 0 °C under N_2 was added dropwise acetone (9.3 g, 0.16 mol). The mixture was stirred for 1 h. The solution was dried with 4A molecular sieves. Distillation gave 2.0 g (13%) of crude isopropylideneisopropylamine: bp 81–93 °C; ^1H NMR δ 1.1 (d, 6 H), 1.85 (s, 3 H), 2.0 (s, 3 H), 3.5–3.7 (m, 1 H).

The above imine (1.8 g, 18 mmol) was dissolved in 10 mL of ether, and the resulting solution was slowly added to a stirred mixture of $LiAlD_4$ (0.45 g, 12 mmol) in 40 mL of ether. After the mixture was stirred for 36 h, the reaction was quenched by the successive addition of 0.45 mL of water, 0.45 mL of 5% NaOH solution, and 1.35 mL of water. The mixture was filtered. Distillation of the filtrate gave 0.86 g (46%) of product: bp 71–75 °C; ^1H NMR δ 0.9–1.11 (m, 12 H), 2.8–3.0 (m, 1 H); mass spectrum, 102 (12, M^+), 87 (100), 58 (21).

***N*-(1-Deuterio-1-methylethyl)-2-deuterio-2-propanamine (Diisopropylamine-*d*$_2$).** Sodium cyanoborodeuteride was prepared in 48% yield from sodium cyanoborohydride following the method of Borch et al.[39] The $NaBD_3CN$ contained <5% protium as judged by ^1H NMR spectroscopy.

Following the general method of Borch et al.,[39] acetone (1.7 mL, 23 mmol), $NaBD_3CN$ (0.78 g, 11.8 mmol), and ammonium acetate (0.85 g, 11.2 mmol) were dissolved in 40 mL of CH_3OD. After the mixture was stirred at ambient temperature for 48 h, concentrated HCl was added to bring the solution to ca. pH 2. The amine salt was dissolved in water, and the solution was extracted with ether. The aqueous phase was neutralized with solid NaOH, and the amine was extracted into ether. The latter ethereal solution was dried with $MgSO_4$, and most of the ether was removed by distillation. The remaining volatiles were transferred by vacuum to give 1.8 g of an ethereal solution that was found by ^1H NMR spectroscopy to contain 19% (220 mg) of diisopropylamine-d_2: ^1H NMR δ 0.95 (s).

Base Solutions. Lithium diisopropylamine (LDA) and lithium *tert*-butylethylamide (LBEA) solutions were prepared and titrated by the method of Vedejs et al.[40]

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(32) Some preliminary studies (Varick, T. R.; Newcomb, M., unpublished results) suggest that H-atom transfer is not coupled to ET in the TCl reductions. The reaction of trityllithium (TLi) with *N*-chlorodiisopropylamine in THF at −78 °C produced triphenylmethane in high yields. When TLi reacted with the monodeuterated chloramine, $(CH_3)_2CHN(Cl)CD(CH_3)_2$, at −78° C, the kinetic isotope effect for the intramolecular competition (k_H/k_D = 2) was virtually indistinguishable from that found when TCl reacted with LDA-d_1 (Table II). This result is best explained by formation of a common radical pair in both reactions.[33]

(33) We should note that initial metal halogen exchange in either reaction to produce the components of the other can be ruled out because it would give a mixture containing TLi and TCl. The powerful reducing agent TLi will react directly with molecular TCl to give trityl radicals and, ultimately, trityl dimer. An electrochemical example of this behavior has been completely characterized.[34]

(34) In direct electrochemical reduction of 9-chloro-9-mesitylfluorene (**8**), the 9-mesitylfluorene anion reduces molecular **8** to the radical and chloride ion; the $R^•/R^-$ couple acts as a homogeneous redox catalyst for **8**: Andrieux, C. P.; Merz, A.; Savéant, J.-M. *J. Am. Chem. Soc.* **1985**, *107*, 6097.

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(36) We note that predissociation of simple alkyl halides in ethereal solvents (i.e. solvolysis to give the strongly oxidizing oxonium ion) followed by ET to the oxonium ion might account for the small amounts of radical initiation that have been observed in reactions of alkyl halides with several nucleophiles.[37]

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Products from Reactions of Trityl Halides with Lithium Dialkylamides. The following procedure is representative. To a 40-mL centrifuge tube fitted with a septum was added 0.5 mL of a 0.55 M LDA (1.1 mmol) solution in THF and 9.5 mL of THF. The solution was cooled to −78 °C, and 0.63 mL of a THF solution containing 0.21 mmol of Ph_3CCl and 55.4 mg of pentadecane was added. After 1 h, the reaction was quenched with 1 mL of methanol and warmed to room temperature. Hexane (5 mL) was added, and the solution was washed with water and brine and dried with $MgSO_4$. A GC yield of triphenylmethane was obtained with pentadecane as an internal standard. The solvent was removed, and the relative yields of triphenylmethane, (4-benzhydrylphenyl)triphenylmethane (**2**), and trityl "trimer" were determined by ^{1}H NMR spectroscopy by comparison of the methine signals at δ 5.55, 5.50, and 5.46, respectively. Dimer **2** was isolated by preparative silica gel TLC (1:2, CH_2Cl_2–hexane elution): mp 221–224 °C (lit.[9a] mp 226–227 °C); ^{1}H NMR δ 5.50 (s, 1 H), 6.89 (d, 2 H), 7.1–7.4 (m, 27 H); ^{13}C NMR δ 56.4, 64.7, 125.9, 126.3, 127.4, 128.3, 128.4, 129.4, 131.6, 131.2, 141.3, 143.9, 144.7, 146.8.

Reaction of Triphenylcarbenium Tetrafluoroborate with LDA. Ph_3CBF_4 (0.0326 g, 0.099 mmol) was weighed into a flask that was then flushed with nitrogen and cooled to −78 °C. Following the addition of 3 mL of THF, 1.5 mL of 0.5 M LDA solution (0.75 mmol) was added. The reaction was quenched after 1 h by addition of methanol. Ether (5 mL) was added, and the resulting solution was washed with water and brine and dried over $MgSO_4$. The product was analyzed by GC (pentadecane standard) and by ^{1}H NMR as described above.

(4-Methoxyphenyl)diphenylmethane (4-H). (4-Methoxyphenyl)diphenylchloromethane (**4-Cl**) (0.23 g, 0.94 mmol) was dissolved in 5 mL of THF. After the solution was cooled to −78 °C, 2.2 mL of a 0.75 M LDA solution in THF (1.65 mmol) was added, and the mixture was stirred for 3 h. The reaction was quenched with 2 mL of methanol, and 5 mL of ether was added. The solution was washed with water and brine and dried over $MgSO_4$. The solvent was evaporated in vacuo to yield 0.20 g (78%) of **4-H**: ^{1}H NMR δ 3.07 (s, 3 H), 5.50 (s, 1 H), 7.0–7.5 (m, 14 H).

Bis(4-methoxyphenyl)phenylmethane (5-H) was prepared in 75% yield from bis(4-methoxyphenyl)phenylchloromethane (**5-Cl**) following the procedure given above: ^{1}H NMR δ 3.07 (s, 3 H), 5.46 (s, 1 H), 7.0–7.5 (m, 14 H).

Kinetic Studies of Reductions of Trityl Chloride by Lithium Dialkylamides. The reactions were similar to the product studies. The solutions contained a 10-fold excess of lithium dialkylamide. Several similar solutions were prepared, and the reactions were commenced simultaneously. Periodically, a reaction mixture was quenched with methanol. Following a workup, the yield of triphenylmethane was determined by GC (pentadecane standard). Each pseudo-first-order rate constant was calculated from the results of 4 or 5 reactions run for varying amounts of time.

Kinetic Study of Reactions of Trityl Chloride with Lithium Azide. The following is representative. Lithium azide (5.7 mg, 0.12 mmol) was weighed into a dried flask, 10 mL of THF was added, and the solution was cooled to −78 °C. To this solution was added 0.125 mL of a 0.048 M TCl solution in THF. At the appropriate time, 1 mL of a 1 M LDA solution was added to trap unreacted TCl. After the mixture was stirred for 0.5 h at room temperature, 1 mL of methanol was added followed by 5 mL of ether. The reaction mixture was washed with water and brine and dried over $MgSO_4$. The yield of triphenylmethane was determined by GC with a pentadecane internal standard. Triphenylmethyl azide was calculated as the difference between the theoretical and actual yield of triphenylmethane. Each pseudo-first-order rate constant was calculated from the results of 4 reactions run for varying amounts of time.

Kinetic Study of Reactions of Trityl Chloride with Methanol. The following procedure is representative. Methanol (3 mL) was added to a solution of 0.21 g (0.75 mol) of TCl and 22 mL of THF at −78 °C. At the appropriate time, the reaction mixture was saturated with anhydrous K_2CO_3, and lithium azide was added to quench the unreacted halide. Yields of triphenylmethyl methyl ether were determined by GC with an internal standard.

Competition Studies. Chloride **4-Cl** (0.3368 g, 0.99 mmol) and TCl (0.2837 g, 1.02 mmol) was dissolved in 4.5 mL of THF, and the solution was cooled to −78 °C. The mixture was stirred, and 0.68 mL of a 0.75 M solution of LDA in THF (0.51 mmol) was added. The solution turned from an orange to a brown color. The reaction was treated with 2 mL of methanol after 3 h. The reaction mixture was warmed to room temperature and stirred for 2 h, and the products were isolated as in the product studies. The relative amounts of the products were determined by ^{1}H NMR spectroscopy by comparing the areas of the methine signals from **4-H** and **2**. The competition between chloride **5-Cl** and TCl was also performed by this procedure.

Isotope-Labeling Studies. The reductions of trityl halides were performed with dideuterated lithium dialkylamides by the procedure given above for the product studies. The reaction mixtures contained at least a 6-fold excess of the base. The triphenylmethane product was isolated from the reaction mixture by radial chromatography (silica gel, 1:2 CH_2Cl_2–hexane elution). The purified product was analyzed by deuterium content by ^{1}H NMR and ^{2}H NMR spectroscopy and mass spectrometry.

Kinetic Isotope Effect Studies. Base solutions containing either $LiNR_2$-d_1 or equimolar amounts of $LiNR_2$-d_0 and $LiNR_2$-d_2 were prepared. TCl or TBr reductions were conducted by the procedure used in the product studies. A 6-fold excess of base was employed. The product triphenylmethane was isolated and analyzed as described above.

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Steric and Electronic Effects on the Conformations and Singlet Oxygen Ene Regiochemistries of Substituted Tetramethylethylenes. The Origin of the Geminal Effect[1]

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Abstract: The reactions of singlet oxygen with 22 allylically substituted tetramethylethylenes have been studied. Steric and electronic effects on the regiochemistries of the ene reactions have been discovered. Large groups and electron-rich groups increase geminal hydrogen abstraction. Molecular mechanics calculations have been conducted and reveal that the site of hydrogen abstraction is correctly predicted by the rotational barriers of the methyl groups.

The ene reaction first explored in detail by Alder[2] 45 years ago involves the reaction of an olefin containing an allylic hydrogen with an unsaturated electron-deficient enophile to give a 1:1 adduct (eq 1). Interest in the ene reaction has been sustained since this

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