appears at dissociation with a NC distance of 1.66 Å.

The following conclusion is now possible. The rearrangement of 2-diazoacetaldehyde to 3-formyldiazirine should occur photolytically more easily than the retro reaction. This agrees with the experimental results on the system 3-diazo-2-oxoindoline/2'-oxospiro[diazirine-3,3'-indoline].[13] However, contrary to these results we find the thermal isomerization also favored from the linear to the cyclic compound.

6. Summary and Outlook

In this work we have clarified the photochemical reaction mechanisms of the molecules diazirine, 3,3-dimethyldiazirine, and 3-formyldiazirine. It can be shown that the step which primarily leads to the reaction stems from the excitation to a $^1n\sigma^*$ state. $^1n\pi^*$ states will be relevant only after further thermal excitation via internal conversion. Nonnegligible intersystem crossing to repulsive $^3n\sigma^*$ surfaces can also lead to reaction.

In agreement with experiment our investigations show that methylene and dimethylcarbene (or propene) appear as the main products of photolysis of diazirine and 3,3-dimethyldiazirine. Diazomethane can appear as a by-product. We further determine that an equilibrium will be formed in the system 3-formyl-diazirine/2-diazoacetaldehyde which should be both photochemically and thermally on the side of the ring if the linear molecule does not dissociate irreversibly. Diradicals and zwitterions are not found in the three reactions studied.

For the synchronous thermal reaction of 3,3-dimethyldiazirine we determine a symmetry-allowed pathway. We may generalize that such symmetry allowed mechanisms should occur in symmetrically substituted diazirines. α-Ketodiazirines should be particularly prone to isomerization.

For a full clarification of photochemical reaction mechanisms of diazirines, other molecules with different substituent groups should be theoretically investigated. Among them are spiro compounds of the type of pentamethylenediazirine as well as α-diazoamides and halogen-substituted diazirines.

MNDO and ab Initio Study of the Reduction of Formaldehyde by Lithium Methylamide

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Abstract: Theoretical methods were used to study the reduction of formaldehyde to methanol by lithium methylamide (LiNHCH₃) as a model for the reduction of ketones to alcohols by lithium dialkylamides. The proposed mechanism involves the formation of a reactant complex composed of a dimer model (LiNH₂:LiNHCH₃) coordinated to formaldehyde through one lithium. A hydrogen β to nitrogen is transferred to the carbon of formaldehyde, forming methoxide which is stabilized by lithium complexation. The reactant complex is predicted to be in a potential minimum 14.1 kcal/mol deep with respect to the complex LiNH₂:LiNHCH₃ plus H₂C=O while the transition structure is 30.6 kcal/mol higher than the reactant complex. The thermodynamic driving force for the lithium-mediated reduction is the formation of the product complex which is 28.8 kcal/mol more stable than the reactant complex. A transition structure was found for nucleophilic addition of the methoxide ion to the C=N bond of the product complex, which would form aminomethoxymethane upon hydrolysis. However, the product complex is favored thermodynamically, and little condensation product is expected under equilibrium conditions. An alternative mechanism was considered in which the reactant complex consisted of the lithium methylamide monomer (rather than dimer) complexed to formaldehyde. The hydride transfer then occurs through a distorted six-membered cyclic transition structure. From a comparison of the two mechanisms, the effect of aggregation is discussed. All predictions refer to the gas phase.

The first report of the reduction of benzophenone by lithium dialkylamides was made by Wittig[1] in 1962. The reaction was originally concluded to proceed via a concerted β-hydride transfer from the base to the ketone. A single electron-transfer mechanism has more recently been proposed[2] based on the observation of various coupling products. It now appears[3] that the original interpretation was correct and that the products from radical precursors are formed from secondary reactions. The following study was undertaken to determine the energetics of a concerted hydride shift mechanism in the gas phase.

Method

Calculations were carried out at the restricted Hartree–Fock level by using MNDO[4] and the GAUSSIAN 82 program series.[5] Full optimizations using a multiparameter search routine[6] were carried out for all geometries

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(4) (a) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899–4907, 4907–4917. (b) Lithium parameterization: Thiel, W.; Clark, T., unpublished results.

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(6) References to basis sets used are collected here. The program package GAUSSIAN 82 was used throughout: Carnegie-Mellon University, Binkley, J. S.; Frisch, M.; Raghavachari, K.; Fluder, E.; Seeger, R.; Pople, J. A.; 3-21G basis: Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. 6-31G* basis: Hariharan, P. C.; Pople, J. A. *Theoret. Chim Acta* **1973**, *28*, 213. Gordon, M. S. *Chem. Phys. Lett.* **1980**, *7*, 163. Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1977**, *77*, 3654.

Table I. MNDO Heats of Formation (kcal/mol) and 3-21+G Total Energies (-hartrees) for Various Monomers and Complexes

|	MNDO(NEV)[a]	3-21+G//MNDO	3-21+G//3-21+G	Δ[b]
		Monomers		
$H_2C=O$	-33.0	113.243 46	113.244 67	0.8
$HN=CH_2$	20.0	93.509 82	93.511 39	1.0
$LiOCH_3$	-58.9	121.286 88	121.293 98	4.4
$LiNHCH_3$	-0.2	101.510 68	101.517 75	4.4
$LiNH_2$	7.9	62.716 49	62.717 18	0.4
H_2NCH_3	-7.2	94.694 14	94.699 21	3.2
$HOCH_3$	-57.4	114.420 68	114.424 46	2.4
$NHCH_3^-$	23.8	94.023 67	94.030 57	4.3
OCH_3^-	-39.8	113.792 34	113.803 43	7.0
$NaNHCH_3$			254.967 89	
$NaOCH_3$			274.745 94	
		Complexes		
$LiNH_2:LiNHCH_3$, **1**	-51.8 (0)	164.328 73	164.340 02	7.1
$LiNH_2:LiOCH_3$	-107.6 (0)	184.100 20	184.117 35	10.8
$LiNHCH_3:O=CH_2$	-51.1 (0)	214.788 36	214.799 16	6.8
$LiOCH_3:HN=CH_2$	-65.5 (0)	214.836 70	214.847 60	6.8
TS_5	-22.4 (0)	214.760 06	214.766 34	3.9
		Complexes		
reactant complex, **2**	-97.5 (0)	277.594 62		
TS_1, **3**	-85.0 (1)	277.582 36	277.595 07	8.0
$SS_2{}^c$, **4**	-34.9 (2)	277.519 99	277.540 11	12.6
TS_3	-53.5 (1)	277.545 91		
TS_4	-71.4 (1)	277.598 55		
product complex, **5**	-104.6 (0)	277.640 49		
$LiNH_2:LiN(H)CH_2OCH_3$	-95.4 (0)	277.621 91		

[a] Number of negative eigenvalues of MNDO force constant matrix. [b] Energy stabilization (kcal/mol) at the 3-21+G level obtained by using the optimized 3-21+G geometry rather than the MNDO geometry. [c] Super saddle point; characterized by two negative eigenvalues of MNDO force constant matrix.

using MNDO. The MNDO parameters used for lithium have been extensively tested for a number of lithium compounds and have been found to be remarkably successful in predicting the preferred mode of lithium complexation.[7-9] Ab initio calculations were carried out by using the 3-21+G basis, a near double-ζ level basis set which has been augmented with a set of diffuse sp functions for all non-hydrogen atoms. These diffuse functions are essential for systems involving the accumulation of excess negative charge.[7c,9-11] In fact, the 3-21+G basis is found[10] to reduce basis set superposition error[12] even more effectively than the 6-31G* basis which includes a set of d orbitals on non-hydrogens. Single-point calculations made by using the 3-21+G basis at the MNDO geometry are indicated by the notation 3-21+G//MNDO. When energies at the 3-21+G level are evaluated at the optimum 3-21+G geometry, the notation 3-21+G//3-21+G is used. The heats of formation for MNDO calculations and total energies for ab initio calculations are presented in Table I, while geometries are presented in Figure 1.

Reduction of Formaldehyde by $LiNH_2:LiNHCH_3$

The reactants in the reduction reaction are expected to be complexed through the electrostatic interaction of electronegative nitrogen or oxygen and electropositive lithium as dimers, trimers, or higher aggregates.[7c,13,15b] In the present study, one reactant

is assumed to be the complex **1**, a model for the dimer of lithium dimethylamide in which three of the four alkyl groups are replaced by hydrogen. The association energy of **1** from monomers is

1
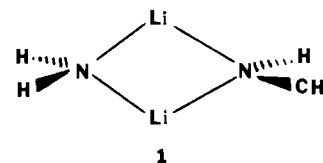
predicted to be 72.4 kcal/mol at the 3-21+G//3-21+G level.[7c,14,15] The second reactant, chosen here as formaldehyde, forms a stable complex with **1** when it approaches one lithium in the approximate plane containing the two lithiums and two nitrogens (**2**, Figure 1b).[16]

2
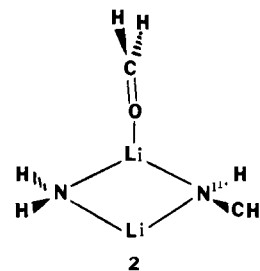
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(14) The dimerization energy of $LiNH_2:LiNH_2$ has been calculated to be 84.4 kcal/mol[9,15] at the 4-31G//4-31G level and 66.5 kcal/mol[7c] at the 3-21+G//3-21+G level.

(15) (a) Hodoscek, M.; Somajar, T. *J. Am. Chem. Soc.* **1984**, *106*, 1854-1856. (b) Kaufmann, E.; Clark, T.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1984**, *106*, 1856-1858.

(16) A similar mode of complexation with formaldehyde has recently been reported with the methyllithium dimer: Kaufmann, E.; Schleyer, P. v. R.; Houk, K. N.; Wu, Y.-D. *J. Am. Chem. Soc.* **1985**, *107*, 5560-5562. For a related investigation, see: Houk, K. N.; Rondan, N. G.; Schleyer, P. v. R.; Kaufmann, E.; Clark, T. *J. Am. Chem. Soc.* **1985**, *107*, 2821-2823.
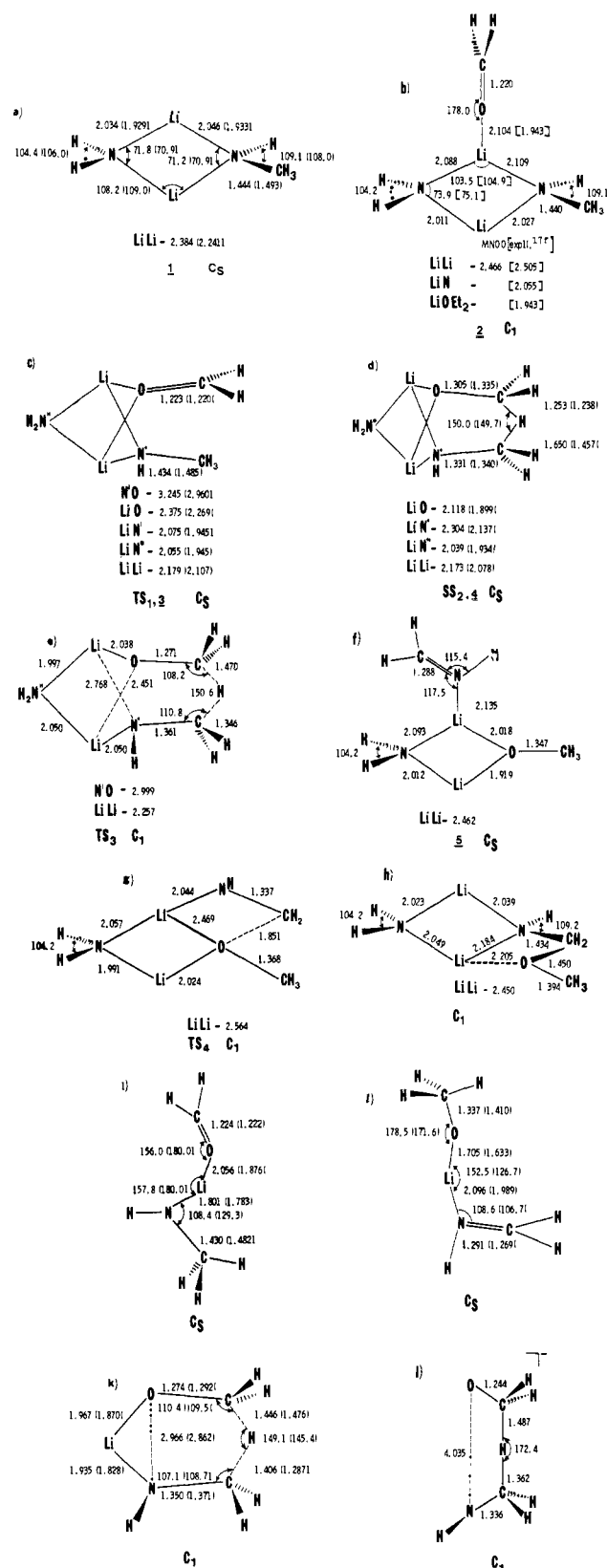
general formula $[(Et_2O)Li\{\mu\text{-}NR_2\}_2Li(OEt_2)]$ in which an ether instead of formaldehyde is bound to each lithium.[17d,f] The N–Li and Li–O distances as well as the LiNLi and NLiN angles in Figure 1b are in good agreement with those from an X-ray structure.[17f] The structure **2** is the lowest energy complex of reactants and will be denoted as the reactant complex.[18]

A transition structure for formaldehyde exchange in the reactant complex occurs when formaldehyde approaches in a direction normal to the approximate plane containing the two nitrogens and two lithiums (**3**, Figure 1c). The barrier to rearrangement at
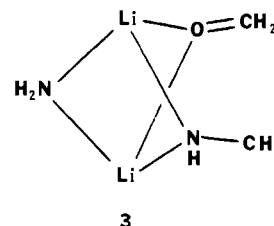
the MNDO level (12.5 kcal/mol) is only slightly less than the association energy of formaldehyde to **1**, while at the 3-21+G-//MNDO level the barrier to rearrangement is about half the association energy (7.7 kcal/mol).

Since structures **2** and **3** are rather close in energy while differing in the coordination number of one of the lithiums, it is important to determine the effect of using geometries optimized at a higher level. Accordingly, the transition structure **3** was fully optimized at the 3-21+G level. A full optimization of **2** was not practical, but a simple method of predicting the effect of using 3-21+G geometries rather than MNDO geometries was devised by assuming additivity of complexation effects. The complexation energy of $LiNH_2$:$LiNHCH_3$ increases 2.2 kcal/mol when one uses 3-21+G geometries rather than MNDO geometries. Likewise the complexation energy of $LiNHCH_3$:$O\!=\!CH_2$ increases 1.5 kcal/mol under the same conditions. Since the reactant complex, **2**, of $LiNH_2$, $LiNHCH_3$, and $O\!=\!CH_2$ has interactions similar to the above simple complexes, the estimated stabilization using 3-21+G rather than MNDO geometries is the sum of the individual stabilizations (3.7 kcal/mol). At the 3-21+G//3-21+G level (and using the approximation for **2** cited above), the association energy of formaldehyde to **1** increases to 15.6 kcal/mol while the calculated rearrangement barrier increases to 9.1 kcal/mol.

The transition structure, **3**, represents a convenient point to compare geometry and energy predictions at different levels. The geometries at the MNDO and 3-21+G levels are given in Figure 1c. There is a clear tendency for the structure to become more compact at the 3-21+G level, although the difference between the 3-21+G energy at the MNDO geometry and the 3-21+G optimized geometry is only 8.0 kcal/mol (Table I). At the MNDO level, struture **3** is predicted to be only 0.2 kcal/mol more stable than to **1** plus $H_2C\!=\!O$. The interactions are more stabilizing at the 3-21+G level where **3** is predicted to be more stable than

Figure 1. Selected geometric parameters and point group for various species at the MNDO and 3-21+G levels. Values for 3-21+G are in parentheses. Text designations are also provided for clarity. Also included in Figure 1b are the values for the X-ray structure of $[(Et_2O)\text{-}Li\{\mu\text{-}NR_2\}_2Li(OEt_2)]$.

The association energy of formaldehyde to **1** is 12.7 kcal/mol at the MNDO level and 14.1 kcal/mol at the 3-21+G//MNDO level. The lithium distances of the complex (Figure 1b) are very similar to several known structures,[17] particularly those of the

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(18) The following reference reports that the stabilization of the reaction $O\!=\!CH_2 + Li^+ \rightarrow LiO\!=\!CH_2^+$ is 35.5 kcal/mol. Del Bene, J. E.; Frisch, M. J.; Raghavachari, K.; Pople, J. A.; Schleyer, P. v. R. *J. Phys. Chem.* **1983**, *87*, 73–78.
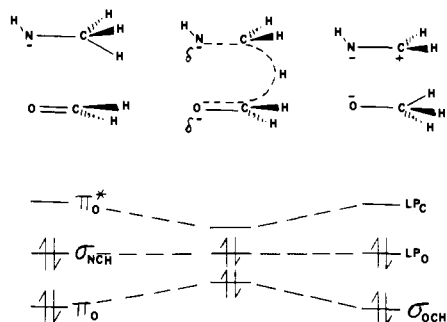
Figure 2. Correlation diagram for the in-plane hydride transfer. The unoccupied π^* orbital of C=O is transformed into an unoccupied lone pair orbital on carbon.

1 plus H_2C=O by 6.4 or 6.5 kcal/mol depending on whether the MNDO or 3-21+G geometries are used.

The reduction step takes places via a hydride transfer from a position β to nitrogen to a position β to oxygen. It is possible that as the hydride is transferred, the oxygen of formaldehyde will adopt an equatorial position in a pseudotrigonal bipyramid. Although the bridging position is less stable in the complex, a methyl hydrogen may be more favorably transferred to formaldehyde in this orientation.

Such a C_s stationary point (**4**, Figure 1d) for the hydride shift was located at the MNDO and 3-21+G levels in which all the substituents of the equatorial nitrogens and oxygen as well as the transferring hydride are in the molecular plane. Since the latter

4
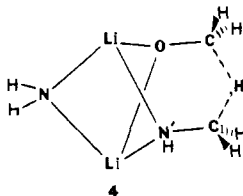
optimization represents the limit of practical optimization using the full basis set (107 basis functions requiring over 180 h of equivalent VAX 11/780 CPU hours for 30 cycles of optimization), it is useful to compare MNDO and ab initio geometries (Figure 1d). Similar to the results obtained for structure **3**, the ab initio results at the 3-21+G level predict that the equatorial ligands come closer together. The hydride transfer involves nearly identical C–H–C angles at both the MNDO and ab initio levels where shortening of the hydrogen bond β to nitrogen in the ab initio structure is accompanied by a shortening of the N–O interaction. Structure **4** is less stable than the reactant complex (**2**) by 46.8 kcal/mol at the 3-21+G//MNDO level and 43.6 kcal/mol at the 3-21+G//3-21+G level (using estimated stabilization of the reactant complex.)

The hydride transfer in **4** is symmetry-allowed as indicated in Figure 2. The three orbitals principally involved are the π and π^* orbitals of formaldehyde and an in-plane σ NCH orbital (β to nitrogen) in structure **3** which transform during the reaction to an empty orbital on carbon, an oxygen lone pair, and a σ OCH orbital (β to oxygen). There should clearly be a favorable rotation of the nitrogen and carbon groups after the hydride is transferred to allow the empty orbital on carbon to interact with the filled nitrogen lone pair. If this rotation becomes favorable along the reaction coordinate before **4** is reached, then this structure will be a stationary point with two imaginary modes (super saddle point).

The vibrational frequencies calculated at the MNDO level for structure **4** revealed two imaginary modes ($1484i$ and $956i$ cm^{-1}). The imaginary mode of $956i$ cm^{-1} corresponds to the hydride shift, while the imaginary mode of $1484i$ cm^{-1} corresponds almost entirely to an out-of-plane motion of the hydrogen α to nitrogen undergoing the hydride transfer. As mentioned, a rotation about the C–N bond would allow a C=N bond to form. Starting from an appropriate guess and minimizing the sum of squares of all gradient components leads to another stationary point (TS$_3$, Figure
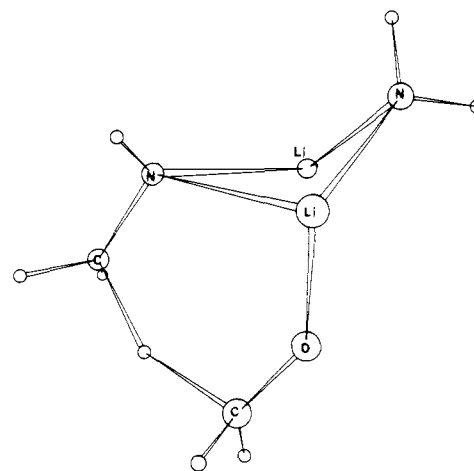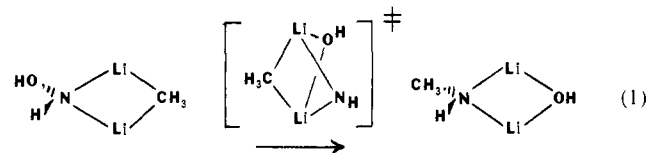

TRANSITION STATE **TS$_3$**

Figure 3. Plot of the MNDO transition state (TS$_3$) for the hydride transfer between the lithium amide dimer (LiNH$_2$:LiNHCH$_3$) (upper moiety) and formaldehyde (O=CH$_2$). Each lithium is strongly coordinated to two atoms and weakly to the third. To increase clarity, the weak coordination of one lithium to oxygen is not indicated by a tapered bond. The transition state has C_1 symmetry.

3) which was confirmed as a transition structure by a force constant calculation which revealed one negative eigenvalue ($1292i$ cm^{-1}). The MNDO reoptimized transition structure, TS$_3$ (Figure 1e), is more open than structure **4** with the NH′ bond rotated approximately 45° to allow better overlap with the forming C=N bond as the hydride is transferred. The equatorial plane containing N′N″O has become skewed with respect to the plane containing the lithiums and N″ (see Figure 1e for N′ and N″ notation). Previously equal in structure **4**, the LiO distances have become 2.038 and 2.451 Å while the LiN′ distances have become 2.053 and 2.768 Å in TS$_3$. The two Li–O distances indicate that the hydride transfer takes place from a transition structure with one lithium oxygen bond clearly more developed than the other. The second Li–O bond strengthens along the reaction path after the transition structure is passed. The barrier with respect to the reactant complex becomes 44.0 kcal/mol at the MNDO level and decreases to 30.6 kcal/mol (Table II) when energies are compared at the 3-21+G//MNDO level.

In a recent study[9] of organolithium amination by lithium alkoxyamides, it was found that an arrangement of lithiums in axial positions and electronegative groups in equatorial positions represented the transition structure to formation of a product complex (eq 1). In contrast to the present study of the reduction of

$$(1)$$

formaldehyde to methoxide, the transition structure (eq 1) involves equivalently forming Li–O interactions.

The most stable complex of the products, LiOCH$_3$, LiNH$_2$, and HN=CH$_2$ is a lithium double-bridged complex (**5**, Figure 1f).

5
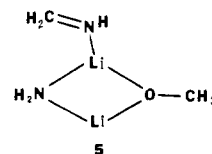
The complex with the carbon of HN=CH$_2$ cis to oxygen is only 0.1 kcal/mol less stable at the MNDO level than the complex with the olefinic carbon trans to oxygen. With MNDO, the product complex is predicted to be 7.1 kcal/mol more stable than the reactant complex (**2**) and 17.0 kcal/mol more stable than the separated LiNH$_2$:LiOCH$_3$ complex plus HN=CH$_2$.[19] The 3-

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Table II. Energies (kcal/mol) Relative to Monomers or Reactant Complex at Various Levels of Calculation

	MNDO	3-21+G// MNDO	3-21+G// 3-21+G	3-21++G// 3-21+G[a]
Association Energies				
LiNH$_2$:LiNHCH$_3$, **1**	-59.5	-63.7	-65.9	
LiNH$_2$:LiOCH$_3$	-56.6	-60.8	-66.6	
LiNHCH$_3$:O=CH$_2$	-17.9	-21.5	-23.0	
LiOCH$_3$:HN=CH$_2$	-26.6	-25.1	-26.5	
Relative Energies				
LiNHCH$_3$:O=CH$_2$	0.0	0.0	0.0	0.0
TS$_5$	28.7	17.4	20.6	20.6
LiOCH$_3$:HN=CH$_2$	-14.4	-30.3	-30.4	-30.6
reactant complex, **2**	0.0	0.0	0.0[b]	
LiNH$_2$+LiNHCH$_3$ + H$_2$C=O	72.0	77.8	81.5[c]	
LiNH$_2$:LiNHCH$_3$ + H$_2$C=O	12.7	14.1	15.6	
TS$_1$, **3**	12.5	7.7	9.1	
SS$_2$, **4**	62.6	46.8	43.6	
TS$_3$	44.0	30.6		
TS$_4$	26.1	-2.5		
product complex, **5**	-7.1	-28.8	-28.6[d]	
LiNH$_2$:LiOCH$_3$ + HN=CH$_2$	9.9	-9.7	-12.0	
LiNH$_2$:LiN(H)CH$_2$- OCH$_3$	2.1	-17.1		
LiNHCH$_3$:O=CH$_2$ + LiNH$_2$	-4.2	56.3	58.5	
LiOCH$_3$:HN=CH$_2$ + LiNH$_2$	-10.2	26.0	28.1	
TS$_5$ + LiNH$_2$	32.9	74.1	79.1	

[a] The 3-21++G basis is created from the 3-21+G basis by the addition of one diffuse s function on each hydrogen. [b] Estimated assuming that the effect at the 3-21+G level of using 3-21+G geometries rather than MNDO geometries for LiNH$_2$:LiNHCH$_3$ (2.2 kcal increase in association energy) and LiNHCH$_3$:O=CH$_2$ (1.5 kcal increase in association energy) is additive. [c] Energies are calculated relative to monomers which are assigned this value so that the estimated relative energy of the reactant complex would be zero. [d] Estimated assuming that the effect at the 3-21+G level of using 3-21+G geometries rather than MNDO geometries for LiNH$_2$:LiNHCH$_3$ (2.2 kcal/mol increase in association energy) and LiOCH$_3$:HN=CH$_2$ (1.4 kcal/mol increase in association energy) is additive.

21+G//MNDO level leads to a greater predicted exothermicity of the overall reaction given above (28.8 kcal/mol), while yielding a similar assocation energy (19.0 kcal/mol). Using the method outlined above for predicting the effect of using 3-21+G geometries rather than MNDO geometries, one obtains an exothermicity of 28.6 kcal/mol and an association energy of 16.6 kcal/mol. The MERP (Minimum Energy Reaction Profile) is presented in Figure 4 for MNDO (Figure 4a) and 3-21+G//MNDO (Figure 4b). The two methods yield similar results. A reactant complex is formed which undergoes a hydride shift to a thermodynamically more stable product complex. The formaldehyde in the reactant complex is reduced to the methoxide ion in the product complex. Abstraction of a proton from the solvent would then yield methanol. Clearly a requirement is that there be a hydrogen β to nitrogen. A similar mechanism would apply to aldehydes and ketones where one or two hydrogens of formaldehyde are replaced by alkyl groups. Different cations should allow complexation but perhaps to differing extents.

A possible reaction which can occur from the product complex is the nucleophilic attack of methoxide on the carbon end of the C=N double bond (Figure 1g). The transition structure (TS$_4$) is 26.3 kcal/mol (Table II) above the product complex at the 3-21+G//MNDO level. A new complex, [LiNH$_2$:LiN(H)C-H$_2$OCH$_3$], which results from the condensation is 11.7 kcal/mol less stable than the product complex (3-21+G//MNDO) and would yield aminomethoxymethane on hydrolysis. Since the

(19) Reference 18 reports that the stabilization of the reaction HN=CH$_2$ + Li$^+$ → LiNH=CH$_2^+$ is 42.8 kcal/mol.

a) LiNH$_2$: LiOCH$_3$+ HN = CH$_2$
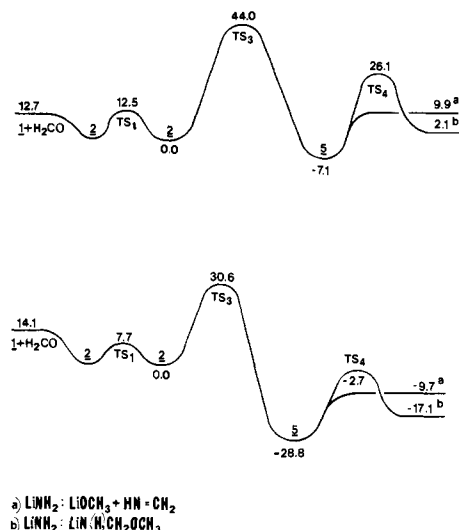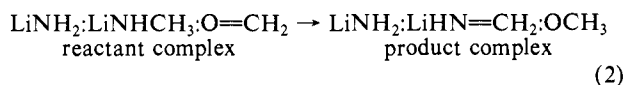b) LiNH$_2$: LiN(H)CH$_2$OCH$_3$

Figure 4. (a) MNDO MERP (Minimum Energy Reaction Profile) for the reduction of formaldehyde by lithium methylamide. (b) 3-21+G-//MNDO MERP where all energies (kcal/mol) are relative to the reactant complex calculated at the specified level.

reverse barrier is low (14.6 kcal/mol; 3-21+G//MNDO), if equilibrium conditions exist, the predominant hydrolysis products will occur from the product complex. The most stable form of the condensation product (Figure 1h) is a C_1 structure in which the ether oxygen preferentially interacts with one of the two lithiums. As noted, above, this tendency is also observed in the reactant complex as well as the transition structure **4**. The interconversion of the two conformers occurs through a transition structure of C_s symmetry with a predicted barrier of 6.5 kcal/mol by MNDO and 6.0 kcal/mol at the 3-21+G//MNDO level. It is interesting to speculate that with the appropriately chosen lithium amide and ketone, the amino ether might be favored.

Reduction of Formaldehyde by Monomeric LiNHCH$_3$

In solutions in which the lithium amide is strongly solvated, the mechanism for reduction of formaldehyde may involve hydride transfer from the complex of formaldehyde with only one lithium amide. This would be true when the solvent–solute interactions are large compared to solvent–solvent and solute–solute interactions. In order to determine the energetics of that mechanism, calculations were carried out and are presented in Tables I and II (complexes are LiNHCH$_3$:O=CH$_2$ and LiOCH$_3$:HN=CH$_2$, while the transition structure is denoted TS$_5$). The geometries of the reactant complex, product complex, and transition structure are given in Figure 1i–k.

The reaction profile involving the lithium amide dimer model reacting with formaldehyde (eq 2) is compared with the reaction between formaldehyde and the simple monomer (eq 3) in Figure 5. The barrier at the 3-21+G//MNDO level is smaller for the

$$\begin{array}{cc} \text{LiNH}_2\text{:LiNHCH}_3\text{:O=CH}_2 \rightarrow \text{LiNH}_2\text{:LiHN=CH}_2\text{:OCH}_3 \\ \text{reactant complex} \quad\quad \text{product complex} \end{array} \quad (2)$$

$$\text{LiNHCH}_3\text{:O=CH}_2 \rightarrow \text{LiHN=CH}_2\text{:OCH}_3 \quad\quad (3)$$

latter reaction (eq 3) than the former (eq 2) (17.4 kcal/mol[21]

(20) For calculations involving sodium, see: (a) Schleyer, P. v. R.; Clark, T.; Kos, A. J.; Spitznagel, G. W.; Rohde, C.; Arad, D.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984**, *106*, 6467–6474. (b) Wurthwein, E.-U.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6973–6978.

(21) At the 3-21+G//3-21+G level the barrier *increases* from 17.4 (3-21+G//MNDO) to 20.6 kcal/mol. It is clear from the forming and breaking bond to hydrogen in Figure 1k that the transition structure is earlier at the 3-21+G//3-21+G level than at the MNDO level. The 3-21+G energy at the MNDO transition structure then represents a point on the potential energy surface beyond the transition structure at the 3-21+G level leading to an underestimation of the barrier. There is very little effect on relative energies when a diffuse s function is added to all hydrogens (Table II).

Table III. Barier Heights and Reaction Enthalpies (kcal/mol) for Hydride Transfer at Various Levels

reaction	barier height	reaction enthalpy			
	3-21+G// MNDO	3-21+G// MNDO	3-21+G// 3-21+G	6-31G*// 3-21+G	MP2/6-31G*// 3-21+G
$H_2C=O + NHCH_3^- \rightarrow HN=CH_2 + OCH_3^-$	5.6 (1.0)[a]	−22.0	−24.8	−17.3	−17.3
$H_2C=O + H_2NCH_3 \rightarrow HN=CH_2 + HOCH_3$		4.4	4.0	7.0	7.6
$H_2C=O + LiNHCH_3 \rightarrow HN=CH_2 + LiOCH_3$		−26.7	−27.0	−18.5	−18.0
$H_2C=O + NaNHCH_3 \rightarrow HN=CH_2 + NaOCH_3$			−28.1	−18.9	−17.1
$H_2C=O + LiNH_2:LiNHCH_3 \rightarrow HN=CH_2 + LiNH_2:LiOCH_3$		−23.8	−27.6		
$LiNHCH_3:O=CH_2 \rightarrow LiOCH_3:HN=CH_2$	17.4	−30.3	−30.4		
reactant complex (**2**) $\rightarrow$ product complex (**5**)	30.6	−28.8	−28.6[b]		

[a] The first value (5.6) is calculated at the MNDO geometry for the hydride transfer in the cis orientation, while the second is for the trans orientation. The cis geometry (Figure 11) is a super saddle point at the MNDO level. [b] Estimated, see text.
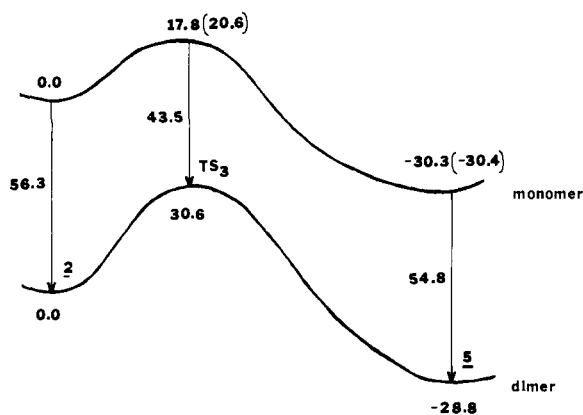

Figure 5. Comparison of reaction profiles for the reduction of formaldehyde by lithium methylamide (top) and by the lithium methylamide dimer model (bottom). The amount of stabilization (kcal/mol) when the second lithium amide is complexed is given beside the vertical arrows.

compared to 30.6 kcal/mol). However, the entire potential energy surface of eq 2 is stabilized through complexation of another lithium amide. The amount of stabilization (given by the vertical arrows in Figure 5) is less for the transition structure than for the reactant and product complexes.

By a simple argument, it should be clear that the reactants and products of eq 3 should be stabilized more in solution than those of eq 2. The number of sites for potential coordination to the solvent in eq 2 is reduced since one of the sites is strongly bound to the lithium amide. Since solvent–solvent interactions for THF (the usual solvent) are less than solvent–solute interactions, increasing the number of interactions of the solvent with lithium amide and the lithium amide–formaldehyde complex should increase the effect of solvation.

The hypothetical effect of solvation on the reaction profile is shown in Figure 6. There are at least three possibilities. First, the effect of solvation can be everywhere less than the stabilization of the second lithium amide (case 1). In this case, the reaction would proceed through eq 2. Second, the effect of solvation could be less than complexation of the second lithium amide for the reactant complex and product complex but would "cross" with eq 3 before reaching the transition structure (case 2). In this possibility, the reaction would begin along eq 3, but as the reactant complex approached the transition structure, the extra lithium amide would be solvated. Possible experimental support for case 2 in a somewhat related system comes from a recent study[22] of the alkylation of 3-methylcyclohexanone *N,N*-dimethylhydrazone in 2-methyltetrahydrofuran (MeTHF). Stereoselective results suggest that the active alkylation agent is a lithium monomer rather than a dimer or aggregate. Third, the "extra" lithium amide would be solvated during the entire reaction profile (case 3). Since lithium amides are known[13c] to aggregate in a variety of solvents

(22) Collum, D. B.; Wanat, R. A. *J. am. Chem. Soc.* **1985**, *107*, 2078–2082.
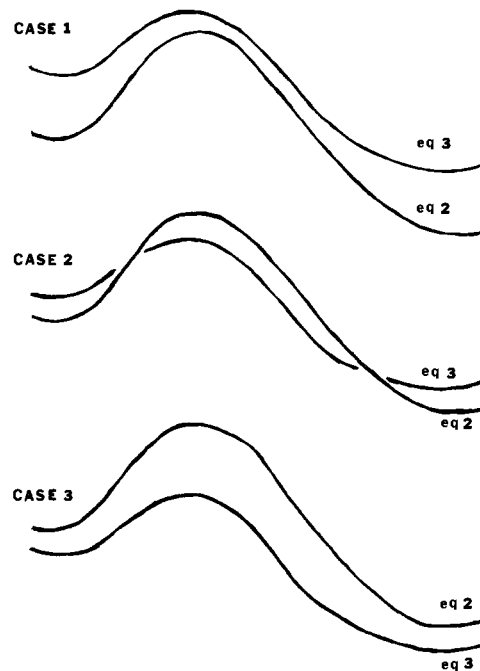

Figure 6. Three possible effects of differential solvation. Case 1 indicates that reaction through the lithium amide dimer is favored. Case 2 indicates that the dimer is favored in the reactant and product complex, but in the transition state the "extra" lithium amide is solvated. Case 3 indicates that the reaction through the lithium amide monomer is favored throughout the hydride transfer. Case 3 is less likely since it is known that lithium amides aggregate in ether solutions.

(Et$_2$O, THF, and others), this last possibility is less likely.

Role of Counterion

To determine what role the cation plays in the hydride shift, the transition structure for intermolecular hydrogen transfer was located at the MNDO level for the reaction of formaldehyde with the methylamide anion. Two orientations were investigated. The hydride transfer in the cis-like orientation is a super saddle point, while the true transition structure is 4.6 kcal/mol lower in energy and is in a trans-like orientation. Since hydride transfer for the complexes occurs through a cyclic transition structure, the cis-like orientation (Figure 11) is probably more appropriate for comparison. The distances around the transferring hydride in the intermolecular pathway are similar to those in the intramolecular pathway (Figure 1k). A comparison is made in Table III of barrier heights for three reactions involving a hydride transfer. The increase in the barrier height as the number of complexing interactions increases is due to a smaller stabilization of the transition structure by Li$^+$ and Li$^+$/LiNH$_2$ relative to reactants.

The effect of the counterions H$^+$, Li$^+$, and Na$^+$ on enthalpies of reaction is presented in Table III. The cations Li$^+$ and Na$^+$ yield very similar enthalpies of reaction compared to the anion value, while the value for H$^+$ is about 25 kcal/mol more endothermic.[20] In the present reaction, the formation of lithium amide

can be thought of as providing the driving force behind the reduction of ketones to alcohols by labilizing the α hydrogen of the amide. The last three entries in Table III indicate that the complexation energy between reactants and between products is nearly equal since the enthalpy of reaction is nearly the same as for monomers.

Conclusion

The barrier for hydride transfer of a methyl hydrogen in $LiNHCH_3$ to formaldehyde has been calculated for the lithium amide–formaldehyde complex and for the complex of the lithium amide dimer model. While the former pathway has a lower barrier (17.8 kcal/mol, 3-21+G//MNDO) than the latter (30.6 kcal/mol, 3-21+G//MNDO), the latter pathway is strongly stabilized through complexation with the additional lithium amide. Unless solvent effects stabilize the former pathway by more than 43.5 kcal/mol relative to the latter, the reaction is predicted to proceed by way of the lithium amide dimer.

While the lithium amide was assumed to be dimeric, the hydride transfer actually may occur from an activated complex in a higher

degree of aggregation. The basic nature of the reaction, however, from such a reactant complex to a more stable product complex is not expected to change. In this regard, it is interesting to note that a recent NMR study[23] of butyllithium aggregates in THF has shown that the dimer is approximately 10 times as reactive as the tetramer toward benzaldehyde, while no evidence for a butyllithium monomer could be found even at low concentrations.

Further studies are under way to explore the mechanism of the reaction of other metalated bases with ketones, in particular the origin of C-substituted and N-substituted products formed from ambient anions.

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An ESR Study of the Reaction of Aluminum Atoms with Buta-1,3-diene: Cheleotropic Cycloaddition and Substituted Allyl Formation[1]

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Abstract: Electron spin resonance spectroscopic studies of the reaction of ground-state aluminum atoms with buta-1,3-diene in adamantane at 77 K in a rotating cryostat have demonstrated the formation of two major paramagnetic products, a σ-bonded aluminum cyclopentene and an aluminum-substituted allyl. The aluminum cyclopentene has the parameters $a_{Al} = 229.8$ G, $a_H(4) = 3.7$ G, $a_H(2) = 2.5$ G, and $g = 2.0025$. This is an example of a cheleotropic reaction, and ab initio MO calculations place the aluminum atom below the plane of the butadiene carbon framework at an angle of about 42°. The aluminum-substituted allyl has the parameters $a_{Al} = 33.5$ G, $a_H(1) = 4$ G, $a_H(2) = 14$ G, $a_H(3) = 11$ G, and $g = 2.0023$ and is possibly a "bridged" species.

Uncertainty still surrounds the nature of the primary products from reaction of ground-state aluminum atoms ($3s^2 3p^1$) with alkenes and alkadienes. Electron spin resonance (ESR) studies of the reaction with ethylene in solid Ar at 4 K indicate a weak π-complex in which the $C=C$ bond remains intact but in which some electron transfer occurs from the full π orbitals to an empty Al 3p orbital and in which the unpaired electron resides mainly in a 3p orbital parallel to the double bond.[2] On the other hand σ-bonded aluminocyclopropanes are indicated by the deuterolysis experiments of Skell et al., who reacted the condensates prepared at 77 K with D_2O.[3] 3,4-Dideuteriobut-1-ene was formed from buta-1,3-diene, indicating interaction with only one double bond of the conjugated system. However, caution must be exercised in elucidating the structures of primary products from such experiments because of the many additional reaction steps from primary to final analyzed product. Differences between the ESR and deuterolysis results could be due, in part, to the large temperature difference in the two experiments which at these low temperatures will accentuate the effects of quite modest differences in energy barriers.

In the present paper we describe the results of our ESR studies of the reaction of Al atoms with buta-1,3-diene and some deuterated and ^{13}C labeled derivatives in a rotating cryostat at 77 K under conditions more akin to those of the deuterolysis experiments. Our work shows the formation of an aluminum cyclopentene with an unusually large aluminum hyperfine interaction (HFI) and the addition of an aluminum atom to the conjugated system to form an aluminum-substituted allyl.

Experimental Section

The rotating cryostat, EPR spectrometer, and methods used to calibrate spectra and calculate spectral parameters have been described previously.[5] The parameters in the Hamiltonian describing the spectra were obtained by diagonalization of the spin matrix and computer simulation of the spectra. Aluminum atoms in their ground electronic state were produced by resistively heating metallic aluminum in a molybdenum

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