

terconversion was examined kinetically. Equilibrium data were obtained at eight temperatures: 217.0 (18.83), 223.5 (17.99), 230.0 (17.30), 236.25 (17.06), 243.0 (16.47), 250.0 (16.08), 257.0 (15.60), and 262.5 °C (15.11), and their rates of interconversion were obtained at six temperatures (Table II).

A van't Hoff plot of the equilibrium data gave a $\Delta H^\circ = 2.38$ kcal/mol and $\Delta S = 0.95$ eu, while the Arrhenius plots of rates gave the least-squares analyses:

$$\log k_1/s^{-1} = 13.4 \pm 0.3 - (39.4 \pm 0.8 \text{ kcal/mol})/[RT \ln 10]$$

$$\log k_{-1}/s^{-1} = 13.2 \pm 0.3 - (41.8 \pm 0.8 \text{ kcal/mol})/[RT \ln 10]$$

Chesick¹² and Baldwin¹³ obtained activation parameters for endo \rightarrow exo isomerizations of similar hydrocarbon systems **9** and **10**. A comparison of these data with ours for **6** \rightleftharpoons **7** clearly



$$\log A = 14.4$$

$$E_a = 39.15 \pm 0.8 \text{ kcal/mol}$$



$$\log A = 15.0$$

$$E_a = 39.2 \pm 0.1 \text{ kcal/mol}$$

indicates that differences in activation energies for endo-exo interconversion for the three systems are insignificant. Thus it would appear that the presence of the four fluorine substituents in **6** has little effect upon the C₁-C₄ bond dissociation energy.

A necessary corollary of such a conclusion is that the observed inhibition of cyclopentene formation observed in the isomerization of **1** must derive from an inhibition of the 1,2-hydrogen shift process of the intermediate 4,4,5,5-tetrafluorobicyclo[2.1.0]pentane-1,3-diyl species (**5**). The source of this unexpected inhibition is presently under further investigation.

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(12) Chesick, J. P. *J. Am. Chem. Soc.* **1962**, *84*, 3250.

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Dominance of the Proximity Effect of Complexation over Resonance and Inductive Effects in Directing a Metalation: Regiospecific β Lithiation of *N,N*-Diisopropylcyclohex-3-enecarboxamide and of *N,N*-Diisopropyl-2-methylpent-4-enecarboxamide

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Complexation between a metal atom of a reagent and a functional group of a substrate usually reinforces that group's effects in subsequent chemistry. For example, recent evidence that association between a carbonyl oxygen and the lithium of an organolithium base is involved in the formation of enolates from ketones¹ and of dipole stabilized carbanions from amides² and formamidines³ can be taken to suggest that resonance, inductive, and proximity effects, enhanced by complexation, are important factors in the deprotonation.^{4,5} In most cases these effects are

Scheme I

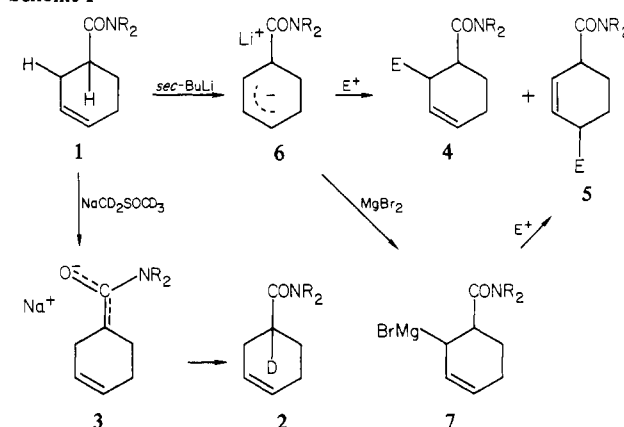


Table I. Lithiation and Substitution of *N,N*-Diisopropylcyclohex-3-enecarboxamide (**1**)

reactant	electrophile	E	4 ^a	5 ^a
6	CH ₃ I	CH ₃	53	18
7	CH ₃ I	CH ₃		95
6	(CH ₃) ₂ CO	(CH ₃) ₂ COH	14	57
7	(CH ₃) ₂ CO	(CH ₃) ₂ COH		90
6	(CH ₃) ₃ SiCl	(CH ₃) ₃ Si	34	13
7	(CH ₃) ₃ SiCl	(CH ₃) ₃ Si		58
6	CH ₂ =CHCH ₂ Br	CH ₂ =CHCH ₂	94	
7	CH ₂ =CHCH ₂ Br	CH ₂ =CHCH ₂	18	72
6	<i>n</i> -C ₅ H ₁₁ I	<i>n</i> -C ₅ H ₁₁	64	28
7	<i>n</i> -C ₅ H ₁₁ I	<i>n</i> -C ₅ H ₁₁	23	68
6	D ₂ O	D (96% <i>d</i> ₁)		29
7	D ₂ O	D (93% <i>d</i> ₁)		94

^a % yields of isolated analytically pure material. ^b 1.5 equiv of MgBr₂ in ether was added and the solution allowed to warm to ambient temperature and recooled to -78 °C before electrophile was added.

complementary and not separable. We now wish to report cases which suggest that the effect of proximity can dominate over resonance and inductive effects in directing deprotonation by a carbonyl group complexed to an organolithium.

Treatment of *N,N*-diisopropylcyclohex-3-enecarboxamide (**1**) with sodium dimethylate in dimethyl-*d*₆ sulfoxide gives the 1-deutero isomer **2** via the expected enolate **3**. However, treatment of **1** with 1.1 equiv. of *sec*-butyllithium/tetramethylenediamine in tetrahydrofuran at -78 °C for 1 h followed by quenching with a number of electrophiles yields, after chromatographic purification, the 2- and 4-substituted products **4** and **5** (Scheme I) in the yields and ratios given in Table I.⁶ The deprotonated intermediate in this sequence **6** is the result of β metalation. If the solution containing **6** is treated with magnesium bromide prior to the addition of the electrophile, the 4-substituted isomer **5** is the only product observed in four cases and predominates in the other two. Moreover, **5** is formed stereospecifically; *N,N*-diisopropyl-*trans*-4-methylcyclohex-2-enecarboxamide is obtained in 95% yield.⁷

(4) The importance of proximity effects has often been suggested in metalations. For discussions of ortho metalations see: Gschwend, H., W.; Rodriguez, H. R. *Org. React.* **1979**, *26*, 1. Beak, P.; Snieckus, V. *Acc. Chem. Res.* **1982**, *15*, 306. Jastrzebski, H. J. T. B.; Van Koten, G.; Konijn, M.; Stam, C. H. *J. Am. Chem. Soc.* **1982**, *104*, 5490. For discussions of β' lithiations of unsaturated amides: Kempf, D. J.; Wilson, K. D.; Beak, P. *J. Org. Chem.* **1982**, *47*, 1610. Tamaru, Y.; Kagotani, M.; Furukawa, Y.; Amino, Y.; Yoshida, Z. *Tetrahedron Lett.* **1981**, 3413 and references cited therein.

(5) The intramolecular juxtapositioning of reactive groups to promote a specific reaction over competitive processes, the proximity effect, is a well-known phenomena. For diverse examples, see: Muetterties, E. *Chem. Soc. Rev.* **1982**, *11*, 283. Breslow, R. *Acc. Chem. Res.* **1980**, *13*, 170.

(6) All new compounds were characterized by analytical and spectral properties.

(7) The ¹³C NMR spectra of the products **5** are consistent with only one stereoisomer. The stereochemistry of *trans*-4-methyl-*N,N*-diisopropylcyclohex-2-enecarboxamide was established by independent synthesis. Cargill, R. L.; Sears, A. B.; Boehm, J.; Willcott, M. R. *J. Am. Chem. Soc.* **1973**, *95*, 4346. Van Bekkum, H.; Kleis, A. A. B.; Masser, A. H.; Medema, D.; Verkade, P. E.; Wepster, B. M. *Recl. Trav. Chim. Pays-bas*, **1961**, *80*, 595.

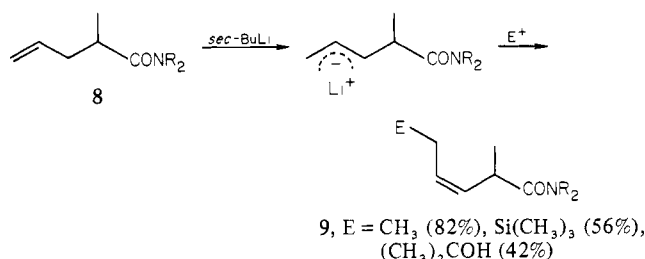
(1) Miller, D. J.; Saunders, W. H., Jr. *J. Org. Chem.* **1982**, *47*, 5039.

(2) Al-Aseer, M.; Beak, P.; Hay, D.; Kempf, D. J.; Mills, S.; Smith, S. G. *J. Am. Chem. Soc.* **1983**, *105*, 2080.

(3) Meyers, A. I.; Reiker, W. F.; Fuentes, L. M. *J. Am. Chem. Soc.* **1983**, *105*, 2082.

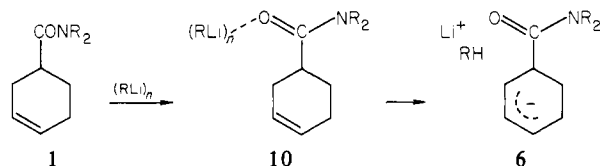
Presumably **6** is converted to **7**, which reacts via a S_E2' process as discussed by Felkin.⁸

The novel β lithiation and regiospecific addition appear to be extendable. The acyclic *N,N*-diisopropyl-2-methylpent-4-ene-carboxamide (**8**) gives the δ -substituted products **9**.^{6,9} The present



approach is convenient and should prove synthetically useful; reactants analogous to **1** are obtained from cycloadditions, and reactants similar to **8** are available by allyl substitution of enolates. Formally related syntheses require dianions of γ,δ -unsaturated carbonyl compounds, multistep sequences, or novel additions and carbonylations of iron carbonyl diene derivatives.¹⁰⁻¹³

The species expected on deprotonation of the amides **1** and **8** are the enolates. Thus, the formation of **3** is rationalized by the customary resonance and inductive effects that operate α to the carbonyl group. The novel β lithiation involving **6** is attributed to reaction via a complex, **10**, that has the organoalkyl base



appropriately positioned to remove the β proton.²⁻⁴ In the lithiations of **1** and **8** a proximity effect overcomes kinetically the more familiar and usually more powerful resonance and inductive effects of the carbonyl group.¹⁴⁻¹⁶ Investigations of useful ex-

(8) The effect of magnesium salts on the regio- and stereochemistry of substitution of allyl systems has been studied, Felkin, H.; Frajerman, C. *Tetrahedron Lett.* **1970**, 1045. Hassel, T.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 399. Biellmann, J. F.; Ducep, J. B. *Org. React.* **1982**, *27*, 1 and references cited therein.

(9) The *Z* stereochemistry is assigned on the basis of a 10.9-Hz coupling of the olefinic protons and assignments of $J_{trans} = 17.5$ and $J_{cis} = 10.6$ Hz in an analogous vinyl group. Romanet, R.; Chemizart, A.; S. Duhoux, S.; and David, S. *Bull. Soc. Chim. Fr.* **1963**, 1048.

(10) For discussion of dieneone dianion derivatives and a summary of other methodologies to provide such substitution, see: Seebach, D.; Pohmakotr, M.; Schrenkenberger, C.; Weidmann, B.; Mali, R. S.; Pohmakotr, S. *Helv. Chim. Acta.* **1982**, *65*, 419.

(11) For anions β to carbonyl groups, see: Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1983**, *105*, 651. Goswami, R.; Corcoran, D. E. *Tetrahedron Lett.* **1982**, 1463. Goswami, R. *J. Am. Chem. Soc.* **1980**, *102*, 5973. Caine, D.; Frobert, A. S. *Tetrahedron Lett.* **1978**, 883. Delomaert, S.; Lesur, B.; Ghosez, L. *Ibid.* **1982**, 4251.

(12) Semmelhack, M. F.; Herndon, J. W.; Springer, J. P. *J. Am. Chem. Soc.* **1983**, *105*, 2497.

(13) A similar β lithiation occurs on treatment of the secondary amide *N*-methylcyclohexenecarboxamide with 2 equiv of *n*-butyllithium: Kempf, D. J.; Beak, P. unpublished results.

(14) The difference in thermodynamic stabilities of the carbanionic species of **3** and **6** can be roughly estimated as $10^{9.2}$. This estimate is based on a ΔpK^a of 9 between a tertiary amide and propene in dimethyl sulfoxide and the fact that an alkyl group has a variable ΔpK^a effect of 1.^{15,16} However, extrapolation to the competitive transition states for deprotonation in the complexes species is uncertain.

(15) The pK^a of *N,N*-dimethylacetamide is estimated at 34-35 by Bordwell and Fried (Bordwell, F. G.; Fried, M. E. *J. Org. Chem.* **1981**, *46*, 4327). The pK^a of propene is estimated as 44 on the basis of the estimation of 42 for toluene by Bordwell, Algrin, and Vanier (Bordwell, F. G.; Algrin, D.; Vanier, N. R. *J. Org. Chem.* **1977**, *42*, 1817) and demonstrations that propene is about 2 pK^a units less acidic than toluene by Boerth and Streitwieser (Boerth, D. W.; Streitwieser, A. Tr. *J. Am. Chem. Soc.*, **1981**, *103*, 6443) and Jaun, Schwarz, and Breslow (Jaun, B.; Schwarz, J.; Breslow, R. *Ibid.* **1980**, *102*, 5741).

(16) Bordwell, F. G.; Bartmess, J. E.; Hautala, J. A. *J. Org. Chem.* **1978**, *43*, 3095.

tensions of this novel lithiation as well as a search for other cases in which proximity effects provide unconventional reaction pathways are under way.

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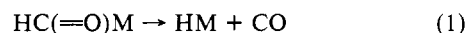
Novel Chain Mechanism for the Formylmetal to Hydridometal Conversion. Free Radical, Photochemical, and Electrochemical Methods of Initiation

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Current interest in formylmetal complexes stems from their potential role as key intermediates in the industrially important catalytic reduction of carbon monoxide.¹ Unfortunately attempts to isolate formylmetal complexes have often led to the corresponding hydridometal complex, i.e.,²



Since the microscopic reverse of eq 1 is uncommon,³ it has not always been rigorously established whether the transformation is thermodynamically or kinetically controlled.

We wish to report a facile kinetic process for the formyl-to-hydride conversion that involves a free radical chain mechanism. The system we scrutinized was the formylrhenate complex *cis*-(OC)₅ReRe(CHO)(CO)₄·Bu₄N⁺ (I), owing to its known thermal stability.^{4,5} Indeed, a thoroughly degassed solution of I in either tetrahydrofuran (THF) or acetonitrile (typically 10⁻¹ M) remained essentially unchanged for several days at 25 °C, provided it was not exposed even to room light. Addition of only 10 mol % of the radical initiator azobis(isobutyronitrile) (AIBN) induced the transformation of I to the corresponding hydride *cis*-(OC)₅ReRe(H)(CO)₄·Bu₄N⁺ (II) in 90% yield⁶ within 4 h, the apparent half-life of I being only 45 min in acetonitrile (and 180 min in THF). The radical chain nature of the AIBN-induced transformation of I to II was also revealed by the marked retardation in rate observed in the presence of 1 equiv of dihydroanthracene ($\tau_{1/2} > 5$ h in acetonitrile), which is known to be an effective hydrogen atom donor.⁷ A turnover number of >500 was calculated from the known rate of AIBN homolysis under these conditions.⁸

The photochemically induced transformation^{4,5} of I to II also proceeds via a radical chain pathway. Thus irradiation of 10⁻¹ M solutions of I in THF at 400 nm afforded II in 75% yield after 3 h ($\tau_{1/2} \sim 30$ min).⁹ By use of ferrioxalate actinometry, the

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(6) Disappearance of I by its ¹H NMR spectrum at 16.1 ppm and appearance of II at -7.2 ppm, using *p*-di-*tert*-butylbenzene as internal standard.^{4,5}

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(9) With Corning (3-74) cutoff or Edmund (405) interference filter.