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 $\Delta H° = 2.38$ kcal/mol and $\Delta S = 0.95$ eu, while the Arrhenius plots of rates gave the least-squares analyses:

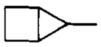
$$\log k_1/\mathrm{s}^{-1} = 13.4 \pm 0.3 - (39.4 \pm 0.8\ \mathrm{kcal/mol})/[RT \ln 10]$$

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

Chesick[12] and Baldwin[13] obtained activation parameters for endo → exo isomerizations of similar hydrocarbon systems **9** and **10**. A comparison of these data with ours for **6** $\rightleftharpoons$ **7** clearly 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 C_1–C_4 bond dissociation energy.

9

$\log A = 14.4$
$E_a = 39.15 \pm 0.8$ kcal/mol



10

$\log A = 15.0$
$E_a = 39.2 \pm 0.1$ kcal/mol

A necessary corrollary 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.

Acknowledgment. The authors acknowledge with thanks the support of this research in part by the National Science Foundation.

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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 ketones[1] and of dipole stabilized carbanions from amides[2] and formamidines[3] 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 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.

Scheme I

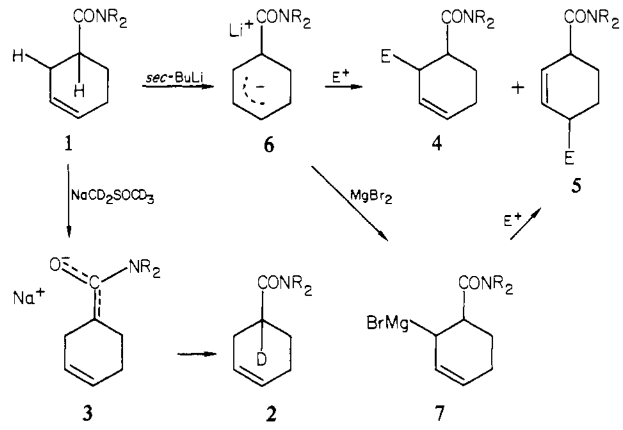

Table I. Lithiation and Substitution of *N,N*-Diisopropylcyclohex-3-enecarboxamide (1)

reactant	electrophile	E	4[a]	5[a]
6	CH_3I	CH_3	53	18
7	CH_3I	CH_3		95
6	$(CH_3)_2CO$	$(CH_3)_2COH$	14	57
7	$(CH_3)_2CO$	$(CH_3)_2COH$		90
6	$(CH_3)_3SiCl$	$(CH_3)_3Si$	34	13
7	$(CH_3)_3SiCl$	$(CH_3)_3Si$		58
6	$CH_2{=}CHCH_2Br$	$CH_2{=}CHCH_2$	94	
7	$CH_2{=}CHCH_2Br$	$CH_2{=}CHCH_2$	18	72
6	$n\text{-}C_5H_{11}I$	$n\text{-}C_5H_{11}$	64	28
7	$n\text{-}C_5H_{11}I$	$n\text{-}C_5H_{11}$	23	68
6	D_2O	D (96% d_1)		29
7	D_2O	D (93% d_1)		94

[a] % yields of isolated analytically pure material. [b] 1.5 equiv of $MgBr_2$ in ether was added and the solution allowed to warm to ambient temperature and recooled to −78 °C before electrophile was added.

Treatment of *N,N*-diisopropylcyclohex-3-enecarboxamide (**1**) with sodium dimsylate 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]

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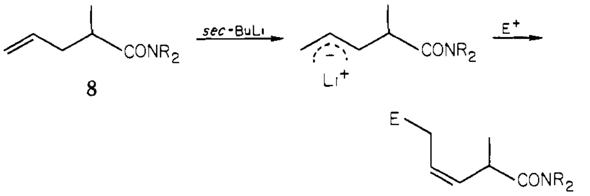
(7) The ^{13}C NMR spectra of the products **5** are consistent with only one stereoisomer. The stereochemistry of *trans*-4-methyl-*N,N*-diisopropylcyclohex-2-enecarboxamide was established by independent synthesis. Cargill, R. L.; Sears, A. B.; Boehm, J.; Willcott, M. R. *J. Am. Chem. Soc.* **1973**, *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.

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-enecarboxamide (**8**) gives the δ-substituted products **9**.[6,9] The present

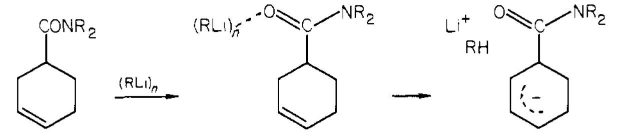


8

9, E = CH_3 (82%), $Si(CH_3)_3$ (56%), $(CH_3)_2COH$ (42%)

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



1 10 6

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

Acknowledgment. We are grateful to the National Science Foundation and the National Institutes of Health for their support of this work.

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(13) A similar β lithiation occurs on treatment of the secondary amide *N*-methylcyclohexenecarboxomide 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 $10^{9\pm2}$. 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).

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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]

$$HC(=O)M \rightarrow HM + CO \qquad (1)$$

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 formyldirhenate complex *cis*-$(OC)_5ReRe(CHO)(CO)_4{}^-Bu_4N^+$ (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*-$(OC)_5ReRe(H)(CO)_4{}^-Bu_4N^+$ (II) in 90% yield[6] 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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(9) With Corning (3-74) cutoff or Edmund (405) interference filter.

0002-7863/83/1505-6351$01.50/0