or P_2O_5 (DMF), and stored in brown screw-cap bottles in the drybox. Pentane (Matheson Coleman and Bell, practical grade) was distilled, and only the fraction boiling below 45 °C was used as an extraction solvent.

Instrumentation. IR spectra were determined on samples in CCl_4 or CS_2 solution in 0.1-mm NaCl cells in a Perkin-Elmer Model 337 grating IR spectrophotometer. NMR spectra were determined on samples in CCl_4 or CS_2 solution in a Varian A56/60A spectrometer at ambient probe temperature (ca. 35 °C). Mass spectra were determined on a Perkin-Elmer Hitachi Model RMU-6E single-focusing instrument with a chamber voltage of 80 V at 200 °C. Most GLC analyses and all GLC separations were performed on a Varian Aerograph Model A90-P3 instrument with a thermal conductivity detector and disc integrator. Some GLC analyses were performed on a Hewlett-Packard Model 5751B instrument with a flame-ionization detector and an electronic chart integrator. Helium was used as the GLC carrier gas.

For most GLC analyses, a column of 10% Carbowax 20M on Chromosorb P or Chromosorb P/AW was used. For some, the column was of 10% SE-54 silicone on Chromosorb P or Chromosorb P/AW. Phenols were analyzed on a column packed with 20% Carbowax 20M with 1.7% of phosphoric acid on Chromosorb P. All yield determinations by GLC were reckoned vs. an internal standard, with account being taken of molar response factors. The internal standard was biphenyl for determinations of oligochlorobenzenes and *p*-chlorophenol for oligochlorophenols.

Conduct of Reactions. Solutions of *t*-BuOK (ca. 0.3 M) were prepared by weighing the *t*-BuOK in the drybox and combining it with a measured volume of HMPA or DMF in the drybox; the solution was placed in a small bottle sealed with a silicone rubber septum and capped with a plastic screw cap in which a 9-mm hole had been drilled to permit withdrawal of solution by means of a hypodermic syringe. Outside the drybox, appropriate amounts of the oligochlorobenzene(s) and of biphenyl (internal standard) were weighed into vials which were capped with a septum and flushed with dry air by using syringe needles as inlet and outlet lines. An appropriate amount of solvent from a septum bottle was added by means of a gas-tight syringe to give a solution 0.15 M in oligohalobenzene.

All transfers and reactions outside the drybox were accomplished with use of septum vials and syringes that had been purged with Drierite-scrubbed air.

Aliquots of the oligohalobenzene solution were introduced by syringe into 10- or 30-mL septum vials. The reactions were started by injecting an equal volume of the base solution into each vial at the recorded time; the vial was immediately shaken to mix the contents. The reaction solutions at the start were 0.15 M in *t*-BuOK and 0.075 M in oligohalobenzene. At a determined time, the reaction was quenched by addition either of a saturated solution of NH_4NO_3 in water or of 0.5 M aqueous sulfuric acid. Also, an aliquot of the *t*-BuOK solution was diluted with water and titrated against standard acid to ascertain its exact concentration.

The reaction solutions were diluted with ca. three volumes of distilled water and extracted with three portions of either diethyl ether or pentane. The combined organic extracts were washed with a little water, and the combined water layers were diluted to a known volume and titrated potentiometrically against $AgNO_3$ with the use of an automatic titrator designed in this laboratory.[30] The organic layers were additionally washed with water, dried over anhydrous Na_2SO_4, and evaporated to remove most of the volatile solvent on the rotary evaporator. The remainder was taken into solution in a little heptane or tetrahydrofuran and analyzed by GLC. If yields of phenolic products were to be determined, the *p*-chlorophenol internal standard was added after quenching of the reaction, and the combined organic layers were extracted with 5% aqueous NaOH or KOH. The basic extract was acidified, the phenols were extracted into pentane or diethyl ether, and the mixture was analyzed by GLC as described.

Every identified product was isolated by preparative GLC and subjected to mass, IR, and NMR spectroscopic analysis, as well as melting point determination when feasible. No new compounds were prepared.

Registry No. **5**, 120-82-1; **6**, 87-61-6; **7**, 108-70-3; **8**, 74986-43-9; **9**, 583-78-8; **10**, 634-90-2; **11**, 576-24-9; **12**, 87-65-0; **13**, 95-94-3; **14**, 608-93-5; 2,3,6-trichlorophenol, 933-75-5; chloride ion, 16887-00-6; *tert*-butyl trichlorophenyl ether, 74986-32-6; *tert*-butyl tetrachlorophenyl ether, 74986-33-7; trichlorophenyl, 25167-82-2; 2,3,5-trichlorophenol, 933-78-8; 2,4,5-trichlorophenol, 95-95-4; 2,3,4,5-tetrachlorophenol, 4901-51-3; 2,3,4,6-tetrachlorophenol, 58-90-2; 2,3,5,6-tetrachlorophenol, 935-95-5; pentachlorophenol, 87-86-5.

(30) Mach, M. H. *J. Chem. Educ.* **1972**, *49*, 125.

Kinetic Formation and Equilibration of Isomeric Ketone Dimethylhydrazone Lithio Anions

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Deprotonation of (*Z*)-[1-^{13}C]-3-pentanone dimethylhydrazone (DMH) ((*Z*)-**1**) by lithium diethylamide and lithium diisopropylamide in THF was studied by ^{13}C NMR spectroscopy. Low regioselectivity was observed, and no isomerization of (*Z*)-**1** to (*E*)-**1** occurred during the deprotonation reaction. Proton-transfer reactions between 3-pentanone DMH (**6**), heptanal DMH (**7**), and 3-heptanone DMH (**10**) and the DMH lithio anions formed by deprotonation of these DMH's at 0 °C were studied by alkylation and GC analysis of the alkylated products. These reactions occurred with half-lives of 2 to >8 h, while the deprotonation of ketone DMH's with lithium dialkylamide bases was complete within 0.5 h at 0 °C. These results show that there is little preference for deprotonation syn or anti to the lone pair of the C=N nitrogen in otherwise equivalent methylene groups in acyclic ketone DMH's.

The regioselectivity of formation of enolates and related anionic intermediates is an important factor in their synthetic utility. Recently, a generalization that deprotonation of imines,[1] nitrosamines,[2] oximes,[3] and tosylhydrazones[4] occurs anti to the lone pair of the sp^2-hybridized nitrogen atom has evolved from reports by several groups. This

(1) Fraser, R. R.; Banville, J; Dhawan, K. L. *J. Am. Chem. Soc.* **1978**, *100*, 7999-8001.

(2) Fraser, R. R.; Ng, L. K. *J. Am. Chem. Soc.* **1976**, *98*, 5895-9.

(3) Kofron, W. G.; Yeh, M. K. *J. Org. Chem.* **1976**, *41*, 439-42. Jung, M. E.; Blair, P. A.; Lowe, J. A. *Tetrahedron Lett.* **1976**, 1439-1442. Lyle, R. E.; Fribush, H. M.; Lyle, G. G.; Saavedra, J. E. *J. Org. Chem.* **1978**, *43*, 1275-6.

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Table I. Lithio Anions Formed by Deprotonation of (Z)-1 in Tetrahydrofuran

base	temp, °C[a]	% 2[b]	% 3[b]
$LiNEt_2$	0	52	48
$LiNEt_2$	−25	65	35
$LiN(i\text{-}Pr)_2$	0	72	28
$LiN(i\text{-}Pr)_2$	−25	74	26

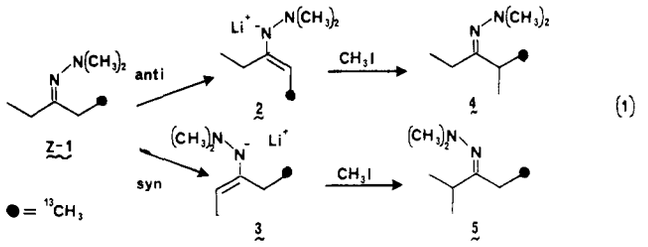
[a] ±2 °C. [b] ±5%.

regioselectivity has been attributed to chelation or electronic effects.[5] An exception to the general observation that deprotonation occurs anti to the nitrogen lone pair is seen in the deprotonation of 3-pentanone dimethylhydrazone (DMH) by lithium dialkylamide bases. We have reported that lithium diethylamide (LDEA) and lithium diisopropylamide (LDA) deprotonate (Z)-[1-^{13}C]-3-pentanone DMH ((Z)-1) with low regioselectivity,[6] and Jung and Fraser have reported that the analogous (Z)-1,1,1-trideuterio-3-pentanone DMH behaves similarly when treated with LDEA.[7] These authors reported that other ketone DMH's isomerize rapidly in the presence of base and speculated that deprotonation of the labeled pentanone DMH's actually occurs anti to the nitrogen lone pair after isomer equilibration.

In this paper we report further studies of the deprotonation of (Z)-1 with lithium dialkylamide bases. Our results show that the deprotonation of (Z)-1 proceeds with low regioselectivity and that isomerization during the deprotonation of (Z)-1 does not occur. In addition, we have found that the deprotonation of a ketone or aldehyde DMH by a ketone or aldehyde DMH lithio anion is much slower than the deprotonation of a ketone or aldehyde DMH by a lithium dialkylamide base. Thus, ketone or aldehyde DMH lithio anion isomers would not be equilibrated by a neutral ketone or aldehyde DMH under normal deprotonation conditions. These results show that generalizations regarding the regioselectivity of kinetic deprotonation of all C=N carbonyl derivatives cannot be made.

Regioselectivity in Deprotonations of (Z)-[1-^{13}C]-3-Pentanone DMH ((Z)-1). We have reported ^{13}C NMR studies which show that (Z)-1 (>95% Z) was deprotonated with low regioselectivity in the presence of LDEA or LDA at 0 °C for 0.5 h to give the DMH lithio anions **2** and **3** by deprotonation anti and syn to the lone pair, respectively (eq 1).[6,8] We now report that when (Z)-1 is treated with excess base at −25 °C, similar low regioselectivity is observed (Table I).

The method for assigning the ^{13}C NMR signals of the labeled methyl groups of **2** and **3** and qualitatively estimating the amounts of **2** and **3** or **4** and **5** has been described[6] and is briefly recapitulated here. By deprotonating both an equimolar mixture of ^{13}C-labeled (E)- and (Z)-1 and a sample of unlabeled **1**, we were able to measure the experimental area ratios for the ^{13}C NMR signals at



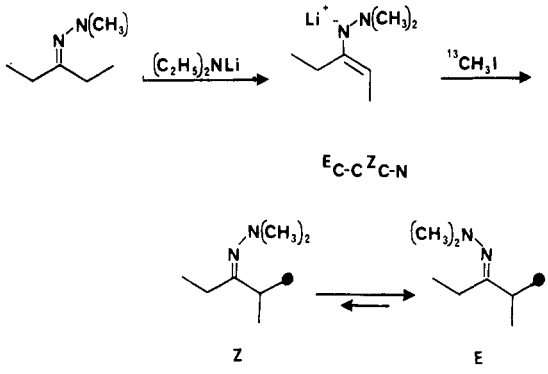
(1)

δ 12.1 and 13.7 arising from an equimolar mixture of **2** and **3** and, after methylation, for the ^{13}C NMR signals at δ 18.9 and 9.7 arising from an equimolar mixture of **4** and **5**. Any differences in relaxation times or NOE effects for the labeled methyl groups of **2** and **3** and of **4** and **5** were corrected by multiplying the measured area ratios by the inverse of the experimentally determined ratios obtained from the equimolar mixtures. When (Z)-1 was deprotonated by LDA at 0 °C, the ^{13}C NMR signals at δ 12.1 and 13.7 were present in a 72:28 (correctd) ratio. Subsequent methylation of this mixture of lithio anions gave a mixture of **4** and **5**, the ^{13}C NMR spectrum of which had signals at δ 18.9 and 9.7 with a corrected area ratio of 75:25, respectively. The large chemical shift difference in the labeled signals from **4** and **5** permits a simple identification; the upfield peak (δ 9.7) must arise from a methyl in an ethyl environment while the downfield peak (δ 18.9) must arise from a methyl in an isopropyl environment. Hence the chemical shifts arising from the mixture of **2** and **3** from LDA deprotonation of (Z)-1 can be assigned as follows: **2** at δ 12.1 and **3** at δ 13.7. The chemical shifts we report here are measured relative to the upfield signal of tetrahydrofuran which we have defined as δ 25.0. Previously we made assignments relative to external Me_4Si which are somewhat different.[6]

Deprotonation of 3-pentanone DMH by lithium diethylamide or lithium diisopropylamide in tetrahydrofuran (THF) at −25 °C is slow enough so that the reaction can be followed by ^{13}C NMR spectroscopy. In a concentrated (ca. 1.5 N) solution of LDEA, 0.13 M (Z)-1 was deprotonated with a half-life of about 5 min. A similar deprotonation of (Z)-1 with LDA had a half-life of about 20 min. For both of these reactions, we were able to observe unreacted (Z)-1 during the course of the deprotonation reaction; no isomerization of (Z)-1 occurred. Figure 1 shows a representative series of spectra obtained in the deprotonation of (Z)-1 at −25 °C by LDEA. Throughout the deprotonation reaction (spectra A–C), no increase in the signal attributable to (E)-1 was observed. Assignments of signals to (E)-1 and (Z)-1 were confirmed by addition of methanol (ca. 3 mmol) which gave a mixture of both (E)- and (Z)-1 in the presence of lithio anions **2** and **3** (spectrum D). Subsequent addition of excess amide base again gave **2** and **3** (spectrum E).

The stereochemistry of the carbon–carbon and carbon–nitrogen bonds of lithio anions **2** and **3** was originally presumed to be $E_{C\text{-}C}$,$Z_{C\text{-}N}$ for both **2** and **3** on the basis of literature precedent. We have now confirmed the carbon–nitrogen bond stereochemistry by reaction of the lithio anion of unlabeled 3-pentanone DMH with ^{13}C-labeled iodomethane (eq 2). The $Z_{C\text{-}N}$ stereochemistry of this lithio anion was confirmed by our observation that the initial [1-^{13}C]-2-methyl-3-pentanone DMH was formed as the less stable Z isomer. Subsequent thermal isomerization in an NMR tube (lithium halide and dialkylamine were both present) produced the thermodynamically favored E isomer. The estimated half-life for this process at 25 °C was ca. 2 h. The assignment of $E_{C\text{-}C}$ stereochemistry of lithio anions **2** and **3** is still an assumption but is

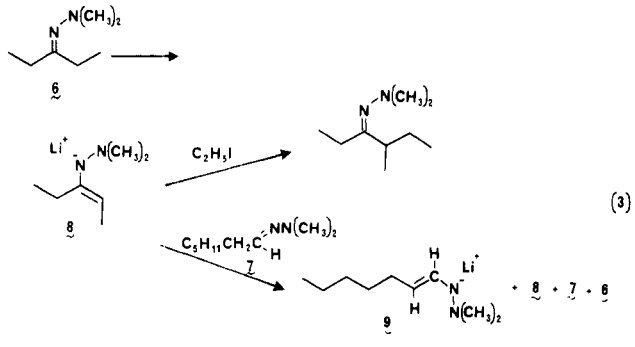
(4) Shapiro, R. H.; Lipton, M. F.; Kolonko, K. J.; Buswell, R. L.; Capuano, L. A. *Tetrahedron Lett.* **1975**, 1811–14.
(5) Houk, K. N.; Stozier, R. W.; Rondan, N. G.; Fraser, R. R.; Chuaqui-Offermanns, N. *J. Am. Chem. Soc.* **1980**, *102*, 1426–9. This paper deals with the stability of various conformations of the anionic species. However, similar conclusions regarding electronic effects in the transition states for deprotonations, although attenuated, would be expected.
(6) Bergbreiter, D. E.; Newcomb, M. *Tetrahedron Lett.* **1979**, 4145–8.
(7) Jung, M. E.; Shaw, T. J. *Tetrahedron Lett.* **1977**, 3305–8. Jung, M. E.; Shaw, T. J.; Fraser, R. R.; Banville, J.; Taymaz, K. *ibid.* **1979**, 4149–52.
(8) ^{13}C NMR spectroscopy has previously been used to study the stereochemistry of DMH lithio anions; cf.: Ahlbrecht, H.; Duber, E. O.; Enders, D.; Eichenauer, H.; Weuster, P. *Tetrahedron Lett.* **1978**, 3691–3694.



probable based on steric considerations and our earlier observations of aldehyde DMH lithio anion stereochemistry.[9] The peak assignments in the ^{13}C NMR spectra of **4** and **5** were confirmed by an independent synthesis of (*E*)-2-methyl-3-pentanone DMH by alkylation of the lithio anion of the DMH of 3-methyl-2-butanone.

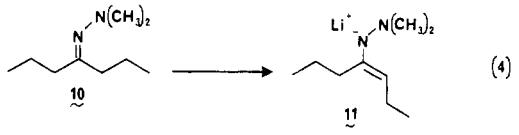
Intermolecular Reactions of DMH Lithio Anions with Neutral DMH's. Deprotonation of a ketone DMH by a ketone DMH lithio anion is one possible mechanism for C–N isomerization of a ketone DMH. We were able to measure crudely the rate of this process in the following manner. A solution of ca. 0.01 M **2** and **3** in the presence of ca. 0.13 M (*Z*)-**1** was made by adding an insufficient amount of LDEA to (*Z*)-**1**. After 9 h at 0 °C, the neutral ketone DMH was found to be present in a ca. 80:20 (*Z*:*E*) ratio. Clearly C–N isomerization is much slower than the deprotonation of (*Z*)-**1** by lithium dialkylamide bases.

The rate of reaction between a ketone DMH and a ketone or aldehyde DMH lithio anion was also studied by addition of a second aldehyde or ketone DMH to a solution of a ketone DMH lithio anion and subsequent analysis of the alkylation products of such reaction mixtures. 3-Pentanone DMH (**6**) was allowed to react with 0.8 equiv of LDA to form a mixture of **6** and **8** as determined by alkylation of an aliquot of this reaction mixture with iodoethane. GC analysis of the product 4-methyl-3-hexanone DMH showed that the deprotonation reaction was complete within 0.5 h at 0 °C. Addition of heptanal DMH (**7**) to the mixture of **6** and **8** and alkylation of aliquots of this new mixture with iodoethane showed that the ratio of lithio anions **8** and **9** (eq 3) was 99:1, 39:61, and 20:80 after 1, 3,



and 8 h at 0 °C, respectively, based either on the relative amounts of unreacted **6** and **7** or the relative amounts of 4-methyl-3-hexanone DMH and 2-ethylheptanal DMH in the alkylated product mixture.

A similar reaction (eq 4) in which the lithio anion formed from 4-heptanone DMH (**10**) was treated with **6** showed that the intermolecular reaction of lithio anion **11** with **6** was also slow. Thus, after 8 h at 0 °C the ratio of **11** to



8 was greater than 4:1, based on the amounts of the ethylated derivatives of **6** and **10**. Reversing the role of the reagents **6** and **10** in this reaction showed that this was not an equilibrium value. Specifically, addition of **10** to lithio anion **8** gave, after 8 h at 0 °C, a 1:6 mixture of anions **11** and **8**, respectively, as determined by GC analysis of ethylated products.

In conclusion, we have shown that the regioselectivity of deprotonation of 3-pentanone DMH by lithium dialkylamide bases is low and the ^{13}C-labeled ketone DMH geometrical isomers do not equilibrate rapidly during such deprotonation reactions. The rate of reaction between a ketone or aldehyde DMH and a ketone DMH lithio anion has been found to be much slower than the rate of deprotonation of a ketone or aldehyde DMH by lithium dialkylamide base. Our results show that generalizations concerning the regioselectivity of deprotonation of acyclic nitrogen derivatives of ketones cannot include dimethylhydrazones and suggest that steric factors may be as important as electronic factors in determining the regioselectivity in these reactions.

Experimental Section

General. All reactions involving organometallic species were run under an inert atmosphere (nitrogen or argon), using routine procedures;[10] all transfers were made by using a syringe. ^1H NMR spectra were recorded on a Varian T-60 spectrometer. ^1H-Decoupled ^{13}C NMR spectra were recorded at 25 MHz on a JEOL PFT-100 spectrometer equipped with a low-temperature apparatus. Temperatures during ^{13}C NMR experiments were measured by using a digital thermometer with a copper-constantan thermocouple in a nonspinning NMR tube containing acetone inserted into the probe of the spectrometer; the thermocouple was kept above the level of the coils. GC analyses were performed on an Hewlett Packard Model 5830A gas chromatograph equipped with a flame-ionization detector, using a 10 ft × $^1/_8$ in. 2% Carbowax 20M on 80/100 Chromosorb G column.

Materials. Commerical (Aldrich) carbonyl compounds (2-butanone, 3-pentanone, 4-heptanone, heptanal) of reagent quality were allowed to react with *unsym*-dimethylhydrazine (Aldrich) by literature procedures[11] to give DMH's in high yield which were purified by distillation. The products from ethylation of DMH lithio anions **8**, **9**, and **11** (4-methyl-3-hexanone DMH, 2-ethylheptanal DMH, and 3-ethyl-4-heptanone DMH, respectively) were made by treating the appropriate DMH (ca. 5 mmol) in THF with 1.1 equiv of LDA at 0 °C for 1 h and subsequent alkylation with 1.1 equiv of iodoethane at 0 °C in a procedure similar to that described below for deprotonation and alkylation of **6**. After a routine workup, the ethylated products were purified by bulb-to-bulb vacuum distillation. ^1H NMR spectra consistent with the assigned structures were obtained for each ketone or aldehyde DMH.

LDA solutions were prepared by adding 1.0 equiv of *n*-butyllithium in hexane (Aldrich) to 1.0 equiv of diisopropylamine (distilled from calcium hydride) in THF (distilled from sodium–benzophenone) at −78 °C. The mixtures were warmed to 0 °C for ca. 10 min and then cooled to −78 °C before use. The preparation of "clean" LDA (2 N) solutions in THF which were suitable for ^{13}C NMR spectroscopic studies was accomplished as previously described.[12] "Clean" LDEA solutions were prepared in a similar manner.

(9) Davenport, K. G.; Eichenauer, H.; Enders, D.; Newcomb, M.; Bergbreiter, D. E. *J. Am. Chem. Soc.* **1979**, *101*, 5654–9.

(10) Brown, H. C. "Organic Syntheses via Boranes"; Wiley-Interscience: New York, 1975.

(11) Corey, E. J.; Enders, D. *Chem. Ber.* **1978**, *111*, 1337, 1362.

(12) Hoobler, M. A.; Bergbreiter, D. E.; Newcomb, M. *J. Am. Chem. Soc.* **1978**, *100*, 8182–5.

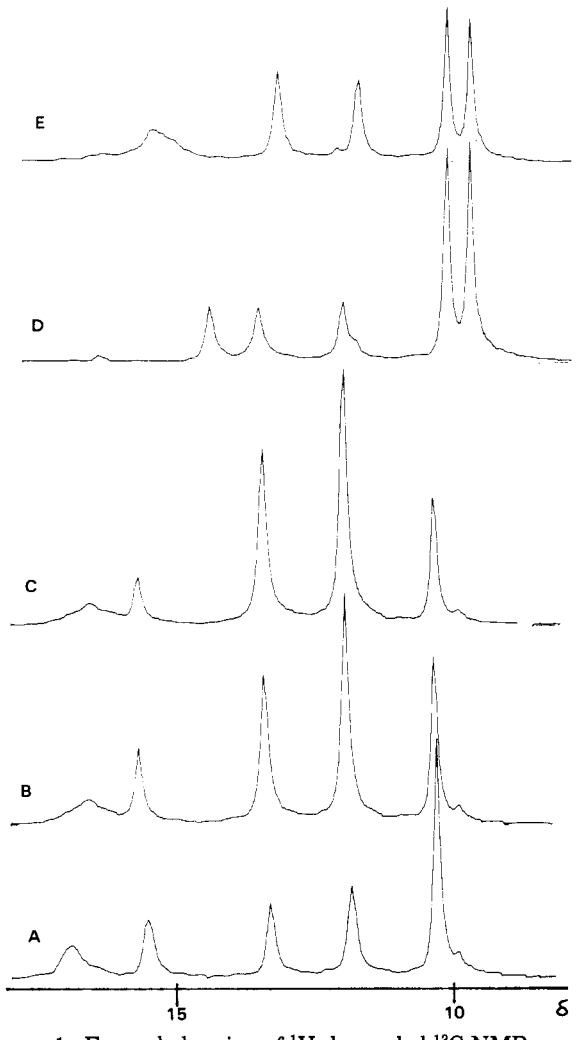


Figure 1. Expanded region of ^{1}H-decoupled ^{13}C NMR spectra recorded at −25 ± 2 °C. (A) Reaction of 30% ^{13}C-enriched (*Z*)-**1** (0.13 M) with LDEA (1.5 N) in THF after 2.5 min. (B) Reaction after 15 min. (C) Reaction after 23 min. (D) Reaction mixture after complete deprotonation and addition of ca. 0.9 equiv of methanol. (E) Reaction mixture D with additional LDEA. The ^{13}C-labeled signals from (*E*)-**1** (δ 9.8), (*Z*)-**1** (δ 10.3), **2** (δ 12.1), and **3** (δ 13.7) are shown. Downfield signals are from the methyl groups in LDEA and diethylamine; the chemical shifts of these signals were observed to vary slightly with changes in concentration of the amine and amide base.

(*Z*)-[1-^{13}C]-3-Pentanone DMH ((*Z*)-1). To a solution of 600 mg (5 mmol) of 2-butanone DMH in 2.5 mL of THF at −78 °C was added 2.7 mL of 2 N "clean" LDA in THF. The mixture was allowed to warm to 25 °C and was stirred for 1 h. The mixture was cooled to −78 °C and a THF solution containing 7 mmol of 30% enriched $^{13}CH_3I$ was added. The mixture (total volume 7 mL) was warmed to 0 °C, and aliquots of the resulting solution were used in ^{13}C NMR studies of the deprotonation of (*Z*)-**1** by LDA. In studies employing LDEA as a base, LDEA was substituted for LDA in the above procedure.

(*Z*)-[1-^{13}C]-2-Methyl-3-pentanone DMH (**4**) was prepared by treatment of the lithio anion of 3-pentanone DMH with ^{13}C-enriched iodomethane at −78 °C by a procedure similar to that described above for preparation of (*Z*)-**1**. The ^{1}H-decoupled ^{13}C NMR spectrum measured at −50 °C contained the labeled ^{13}C signal at δ 18.9. After 2 h at 25 °C, two signals were present for the labeled ^{13}C position (δ 18.9, 19.6) in a 1:1 ratio. After 3 days at 25 °C, the signals at δ 18.9 and 19.6 were present in a 30:70 ratio and were assigned to **4** and **5**, respectively.

^{13}C NMR Studies. A solution of 2 mL of 2 N "clean" base in THF was added to an NMR tube. After the solution was cooled to −78 °C, a solution of (*Z*)-**1** (0.5 mL, 0.4 mmol of (*Z*)-**1**) was added (vortex stirring). After addition of benzene-d_6 (200 μL), the tube was placed in the thermostated probe of the ^{13}C NMR spectrometer and spectra were recorded periodically. Comparison of the integrated areas for the methyl peaks of interest in (*E*)-**1**, (*Z*)-**1**, **2**, and **3** with those obtained by using either an equal mixture of labeled (*E*)- and (*Z*)-**1** or an unlabeled sample of **1** as starting material allowed us to correct for differences in relaxation rates and nuclear Overhauser effects as described in the text.

Previously, we used external Me_4Si as a reference, but we now note that chemical shifts are slightly altered, depending upon the milieu. In this study we have used the β-carbon of THF (defined at δ 25.0) as an internal reference. In the presence of LDA or LDEA, signals from the ^{13}C-labeled positions in (*Z*)-**1**, (*E*)-**1**, **2**, and **3** occur at δ 10.3, 9.8, 12.1, and 13.7, respectively. In our communication, we inverted the assignments for (*E*)- and (*Z*)-**1**.[6]

Reactions between DMH Lithio Anions and Neutral DMH's. The following procedure is representative. A 5-mL THF solution containing 4.5 mmol of **6** and 0.41 mmol of *n*-tridecane was cooled to −78 °C, and 4.0 mequiv of LDA in 5 mL of THF was added dropwise. The resulting mixture was warmed to 0 °C and stirred. Aliquots (1 mL) of this reaction mixture were removed at 0.5 and 1 h and were added at 0 °C to 1 mmol of iodoethane in 1 mL of THF. The resulting mixture of alkylated product and starting materials was quenched with water and diluted with ether. The organic layer was washed with saturated aqueous sodium chloride solution and dried ($MgSO_4$). The solutions were analyzed by GC and the concentration of **6** and 4-methyl-3-hexanone DMH relative to tridecane was measured, using predetermined weight factors. A 5-mL THF solution of 5 mmol of **10** was then added to the mixture of **6** and **8** at 0 °C. At various times, 1-mL aliquots of this mixture of **6**, **8**, **10**, and **11** were removed, ethylated, and worked up as described above. GC analysis as described above was used to determine the amounts of **6** and **10** and their ethylated products.

(*E*)-2-Methyl-3-pentanone DMH was prepared by methylation of (*E*)-3-methyl-2-butanone DMH according to literature procedures.[11] A cold workup and removal of solvent at reduced pressure yielded crude (*E*)-2-methyl-3-pentanone DMH.

Acknowledgment. This research was supported by a grant from the National Institute of Health (GM 26268).

Registry No. (*E*)-**1**, 75031-54-8; (*Z*)-**1**, 75031-55-9; **2**, 75031-56-0; **3**, 75031-57-1; **4**, 75031-58-2; **5**, 75031-59-3; **6**, 16795-73-6; **7**, 67660-53-1; **8**, 70113-25-6; **9**, 75031-60-6; **10**, 14090-58-5; **11**, 75031-61-7; LDA, 4111-54-0; LDEA, 816-43-3; 2-butanone DMH, 5758-05-4; (*E*)-2-methyl-3-pentanone DMH, 75031-62-8; (*E*)-3-methyl-2-butanone DMH, 19885-66-6.