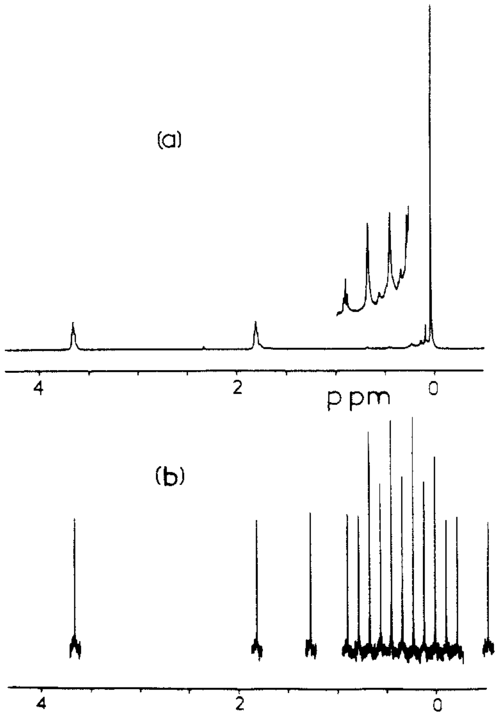
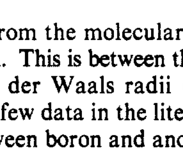


**Figure 1.** (a) $^{1}$H NMR spectrum of **2** obtained with a Bruker WM 360 spectrometer; (b) $^{6}$Li{$^{1}$H} spectra with irradiation centered at various positions in the proton spectrum. The $^{6}$Li spectra contained 8 K data covering 1805 Hz, giving a digital resolution of 0.44 Hz per point. Line widths were all ca. 1.2 Hz.

correlation time found from the molecular volume we obtained a Li···H distance of 2.2 Å. This is between the sum of the covalent and the sum of the van der Waals radii (1.71 and 3.0 Å, respectively).[10] There are few data in the literature on compounds with ($\mu$-H)$_3$ bridges between boron and another element but our results for **2** (Li···B 2.19, Li···H 2.2 Å) are similar to those for Zr(BH$_3$)$_4$ (Zr···B 2.31, Zr—H 2.21 Å) where the bridging hydrogens have been located by electron diffraction.[11]

Hydro[tris(trimethylsilyl)methyl]metalates of aluminum, gallium, and indium have also been isolated.[12] The $^{6}$Li spectra showed sharp singlets, but the signals for the metal hydride protons in the $^{1}$H spectra were too broad to be clearly detected. In each case, however, when the $^{1}$H region was irradiated successively at 180-Hz intervals there was a strong NOE on the $^{6}$Li signal, apparently generated by broad signals at $\delta_H$ (width at half-height (Hz) in parentheses) Al 3.25 (950), Ga 3.25 (2340), and In 4.75 (900). Thus these compounds, like **1** and **2**, appear to exist in toluene or THF with hydrogen bridges between M and Li. It is not possible from NOE measurements to determine how many hydrogen atoms are involved in each bridge, but from integration of THF and Me$_3$Si signals in the $^{1}$H spectra, Li analyses, and molecular weight determinations, the structures do not appear to be completely analogous to that found for **1**. The presence of ($\mu$-H) bridges in the indium compound **3** has been confirmed by an X-ray study;[12] the structures of the aluminum and gallium compounds are being investigated.



**3**

This work shows that selective $^{6}$Li{$^{1}$H} NOE experiments have potential (a) for the detection of weak broad resonances in $^{1}$H spectra and (b) for location of Li atoms relative to hydrogen atoms in organometallic compounds or hydrides. Both the reactivity and the regioselectivity of alkali metal hydrometalate reducing agents are known to depend on the alkali metal as well as the hydrometalate,[13] and it is likely that part of the explanation lies in the presence of species having the alkali metal close to the hydrometal center, probably in hydrogen-bridged species.

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## Asymmetric Induction via Addition–Elimination Process: Nitroolefination of $\alpha$-Substituted Lactones[1]

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Enantioselective construction of quaternary carbon centers is a stimulating subject in syntheses of complex natural products. Because of this, a number of methods to produce quaternary carbons in a highly enantioselective manner have been reported recently.[2] Here, we wish to report a new method for a chiral synthesis of quaternary carbon centers through the addition–elimination process using a chiral leaving group.

Advantage of asymmetric induction of chiral leaving groups includes the direct formation of chiral products, where the removal of the chiral auxiliary in the later stage is unnecessary. This type of chiral induction has lately attracted considerable attention from both mechanistic[3] and synthetic[4] points of view. Particularly, syntheses of chiral binaphthyls by nucleophilic aromatic substitution reported by Wilson and Cram[4c,d] are interesting, because the process involves ipso addition of arylmetal reagents in the initial stage before the elimination of the chiral group occurs. To the best of our knowledge, this was the first example of the chiral induction through an addition–elimination sequence in one pot. We describe another example of the same type of the chiral induction which is the first case in aliphatic systems.

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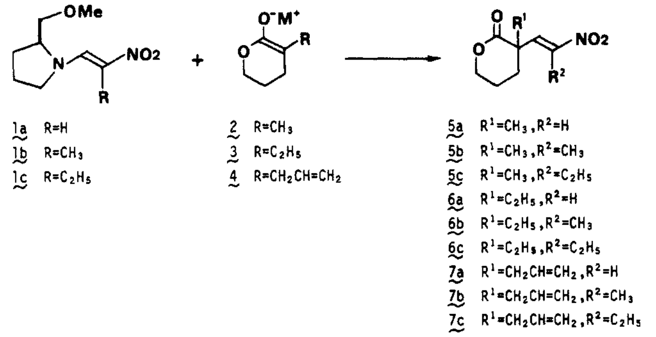
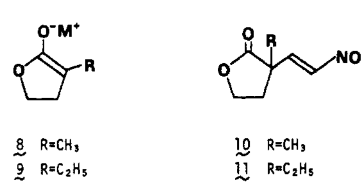
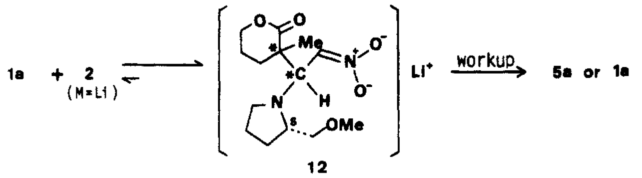
We have chosen nitro enamines **1a–c**[5,6] as a chiral starting material because nitro enamines[8] have been known to react with a variety of nucleophiles affording addition–elimination products.[9] Moreover, $\alpha,\beta$-unsaturated nitro groups are a versatile moiety for further transformations.[10] The reaction of nitro enamine **1a** with enolate **2** (M = Li, 3 equiv) in dimethoxyethane–ether (4:3) at −78 °C yielded **5a** rich in (−)-isomer (run 1 in Table I). Counter cations have a remarkable effect on the reaction. Both the chemical yield and the enantiomeric excess (ee) were increased when $Zn^{2+}$ was used as a countercation (runs 1–3 in Table I). The similar tendency was observed in the reaction of the enolate **3** with **1a**. Thus, $Zn^{2+}$ was chosen as a countercation and reactions of $\delta$-lactone enolates **2–4** with nitro enamines **1a–1c** were performed. The results are compiled in Table I. Substituted nitro enamines **1b,c** gave better results than the parent nitro enamine **1a** in terms of the % ee.





To gain an insight into the origin of the asymmetric induction, the reaction of lithium enolate **2** (M = Li) with nitro enamine **1a** was studied in more detail. The crossover experiment[11] proved that addition of lithium enolate **2** onto nitro enamine **1a** was readily reversible. Quenching conditions are important to obtain a good yield of the product. Thus, starting nitro enamine **1a** was recovered without any trace of the desired product **5a** when the reaction was quenched by pouring into ice–water. However, quenching the reaction by addition to a solution of $p$-toluenesulfonic acid in dichloromethane–THF (4:1) at room temperature yielded **5a** without any detectable amount of the starting nitro enamine **1a**.



12

**Table I.** Asymmetric Nitroolefination of Lactone Enolates via Addition–Elimination Sequence

| run | nitro enamine | counter-cation | enolate[a] | product[b] | yield, % | $[\alpha]^{20}_D$ $CHCl_3$ | % ee[c] |
|---|---|---|---|---|---|---|---|
| 1 | **1a** | $Li^+$ | **2** | **5a** | 50 | −5.4 | 41 |
| 2 | **1a** | $Cu^+$ | **2** | **5a** | 76 | −9.7 | 70 |
| 3 | **1a** | $Zn^{2+}$ | **2** | **5a** | 99 | −12.3 | 86 |
| 4 | **1a** | $Li^+$ | **3** | **6a** | 56 | +8.3[d] | 35 |
| 5 | **1a** | $Cu^+$ | **3** | **6a** | 42 | +0.71 | 82 |
| 6 | **1a** | $Zn^{2+}$ | **3** | **6a** | 99 | +0.69[e] | 82 |
| 7 | **1a** | $Zn^{2+}$ | **4** | **7a** | 63 | −24.8 | 88 |
| 8 | **1b** | $Zn^{2+}$ | **2** | **5b** | 69 | −50.8 | 93 |
| 9 | **1b** | $Zn^{2+}$ | **3** | **6b** | 65 | −25.7 | 90 |
| 10 | **1b** | $Zn^{2+}$ | **4** | **7b** | 54 | −54.3 | 92 |
| 11 | **1c** | $Zn^{2+}$ | **2** | **5c** | 87 | −46.1 | 85 |
| 12 | **1c** | $Zn^{2+}$ | **3**[f] | **6c** | 89 | −37.2 | 96 |
| 13 | **1c** | $Zn^{2+}$ | **4** | **7c** | 69 | −67.8 | 96 |
| 14 | **1a** | $Cu^+$ | **8** | **10** | 82 | −21.3 | 56 |
| 15 | **1a** | $Zn^{2+}$ | **9** | **11** | 72 | −22.6 | 63 |

[a] Three equivalents of enolate were used unless otherwise stated. [b] Absolute stereochemistry of the major enantiomer was not determined. [c] Determined by 400-MHz $^1H$ NMR with $Eu(hfc)_3$. [d] Determined at 435 nm. [e] +20.2° at 435 nm. [f] Six equivalents of enolate were used.

These facts indicate that an equilibrium mixture of the adducts **12** exists in the reaction medium and elimination of either the prolinol or lactone moiety takes place depending upon the workup procedure. The observed asymmetric induction, therefore, depends upon the thermodynamic stabilities of the four possible isomers of adduct **12** arising from the addition of enolate **2** (M = Li) to nitro enamine **1a**. The similar crossover experiment using zinc enolates **2** and **3** showed that the addition of zinc enolate **2** to nitro enamine **1a** was no more reversible. Thus, the asymmetric induction is controlled kinetically, where the addition of the enolate decides the absolute stereochemistry of the product when zinc enolate **2** is used.

In conclusion, we have developed the new method for the construction of a chiral quaternary carbon center. The remarkable feature of this asymmetric synthesis consists in the direct formation of the enantiomer in one pot with high ee. Attempted application of this method to other substrates such as $\alpha$-substituted ketones, esters, and amides proceeded but failed to yield high ee.

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[5] These compounds are easily prepared from the corresponding 1-morpholino-2-nitro olefins[7] and ($S$)-2-(methoxymethyl)pyrrolidine in methanol in more than 90% yield.

[6] Satisfactory spectral data and elemental analyses were obtained for all new compounds.

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[11] Lactones **5a** (30%) and **6a** (49%) were obtained when **3** (M = Li, 1.5 mmol) was added to a reaction mixture of **2** (M = Li, 1.5 mmol) and **1a** (0.5 mmol). On the other hand, **5a** (76%) was obtained as a sole product when the same reaction mixture was quenched before the addition of **3** (M = Li). Yields were determined by HPLC with phenanthrene as an internal standard. The formation of **6a** through addition of **3** (M = Li) to **5a** followed by elimination of **2** (M = Li) was not recognized in a separate experiment.

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## Evidence of Tautomerism in a Triply $^{15}N$ Labeled Monoacetylporphyrin in NMR: Kinetic HH/HD Isotope Effects and Thermodynamics in $CD_2Cl_2$

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Little is known about the influence of the shape of the double-minimum potential on rate constants of hydrogen migration in porphyrins.[2-9] Although qualitative information on tautom-

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