

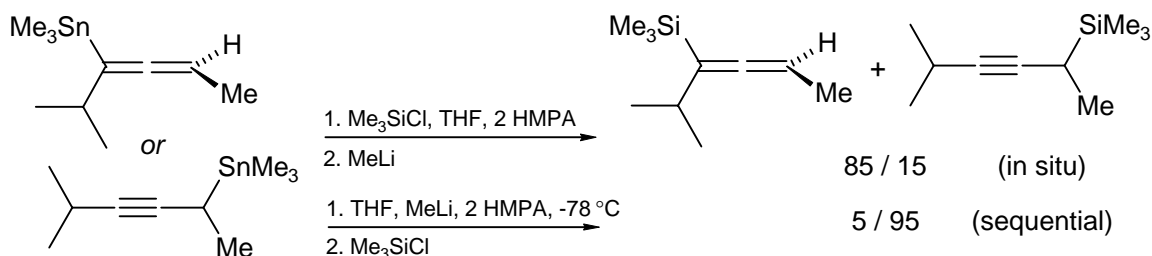
Identification and Mechanistic Consequences of Contact and Solvent-Separated Ion Pair Structures in Organolithium Chemistry

Hans J. Reich,* Aaron W. Sanders, Martin J. Bevan, William H. Sikorski, Robert R. Dykstra
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

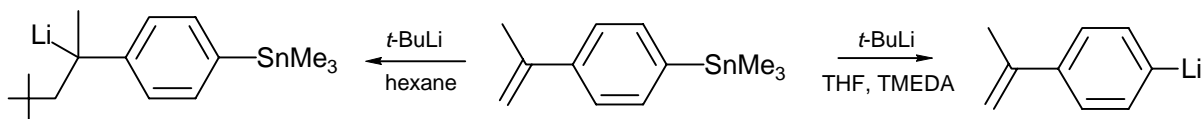
Introduction.

The reactivity of organolithium reagents often shows complex solvent and cosolvent dependence. Fig. 1 shows a few examples where the order of addition of reagents, or addition of a polar cosolvent like tetrahydrofuran (THF), tetramethylethylenediamine (TMEDA) or hexamethylphosphoric triamide (HMPA) causes a dramatic change in the stereochemistry or regiochemistry of reactions.

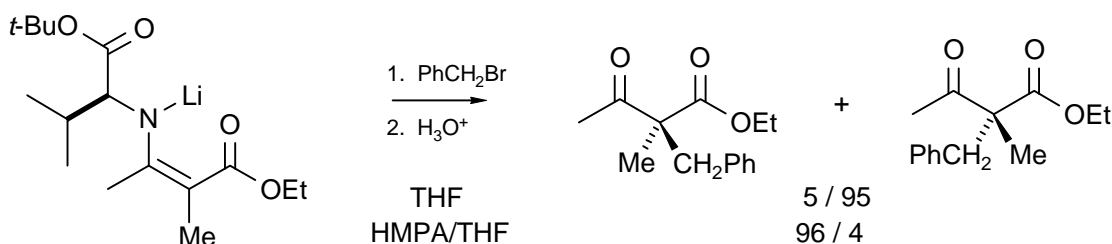
Different products from sequential and *In Situ* Li/Sn exchanges.^[1]



Selectivity between olefin addition and Li/Sn exchange.^[2]



Stereochemistry of alkylation as a function of solvent.^[3]



Selectivity between conjugate addition and substitution.^[4]

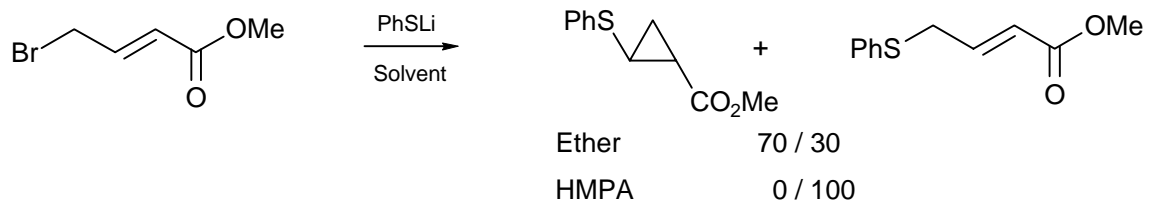
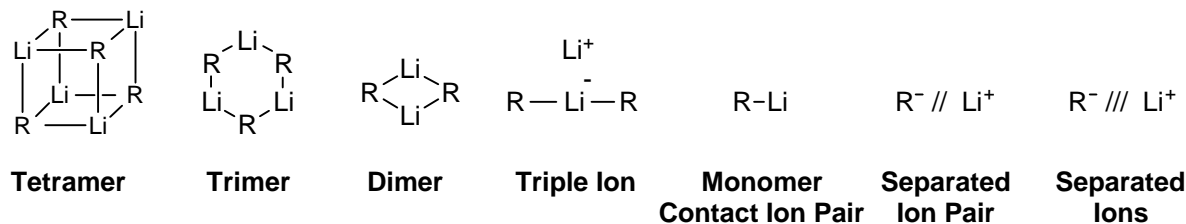


Figure 1. Solvent and other effects on selectivity of organolithium reactions.

Such effects have usually been attributed to changes in the aggregation states and solvation of the lithium species involved. It is well established that many organolithium reagents form various aggregates in ethereal solutions, and that stronger coordinating solvents tend to move the average aggregation state to lower numbers. This is in part because solvents with a higher dielectric constant can better support charge separation, but mainly because the lower aggregates can be more heavily solvent coordinated than higher ones. Since lithium shows a strong propensity for tetracoordination,^[5] cubic

tetramers can coordinate only a single solvent at each lithium, dimers can coordinate two, and monomers three. The biggest structural change occurs when the carbon-lithium bond is broken and the contact ion pair (CIP) monomer is converted to a separated ion pair (SIP), and the most dramatic reactivity effects would be expected as a result of this change.^[6] It is the CIP/SIP dichotomy that is the focus of this paper.



The key role of the CIP/SIP dichotomy in carbanion chemistry was first identified during kinetic studies of the anionic polymerization of styrene, where changes in ion pair structure actually lead to a negative temperature coefficient of the polymerization rate at some temperatures.^[6, 7] Careful UV spectroscopic studies were used to identify the transition from CIP to SIP for a number of conjugated carbanionic species (e.g., lithium fluorenyl^[8, 9] and triphenylmethyl^[10]). Unfortunately, until recently little information about this crucial structural feature was available for the vast majority of lithium species used by synthetic organic chemists. In the absence of well-defined UV/visible absorptions (i.e., a highly conjugated carbanion) it was difficult to reliably detect or quantitate their ion pair status (CIP or SIP). For example, solutions containing separated ion pairs show no conductivity, and molecular weight determinations can distinguish them from dimers and higher aggregates, but not from monomers. The interpretation of UV-VIS absorption,^[8, 9, 10] IR frequency^[11] and NMR chemical shift data^[12, 13, 14] is difficult since often only small shifts in frequency are observed, which do not allow firm conclusions about their origin in terms of the CIP to SIP transition.

Results and Discussion

Distinguishing CIP from SIP Organolithium Species by NMR Spectroscopy. NMR spectroscopic studies have provided a wealth of information to identify various aggregates, and in some cases to prove the existence of monomeric CIP species by the observation of *J* coupling between ⁶Li or ⁷Li^[15] and ¹³C,^[16, 17, 18, 19] ³¹P,^[20, 21, 22] ⁷⁷Se,^[20] ²⁹Si^[23] or ¹¹⁹Sn.^[24] Unfortunately, when the nucleus bonded to Li has no useful NMR properties (O, S, Cl, Br, I and many others), when the couplings are too small, or when dynamic exchange destroys the coupling^[25] only weak inferences about the ion pair structure can be drawn from NMR spectra (for example, by analysis of chemical shift changes in the lithium, proton, or carbon NMR spectra^[12, 13, 14]).

The HMPA titration technique which we developed several years ago^[25] provides a general method for detecting and securely identifying SIP species where the solvating agent is HMPA. Increments of HMPA are added to a sample of a lithium reagent dissolved in mixtures of THF, ether and/or dimethyl ether, and ⁶Li, ⁷Li, ³¹P and ¹³C NMR spectra are measured. Key to the experiment is the detection of Li-P *J*-coupling, which becomes routinely possible at temperatures below -115 °C. Fig. 2 shows sample ⁷Li and ³¹P NMR spectra of CIP 2-methyl-2-lithiodithiane (**1**) in the presence of 1 equiv. of HMPA, and typical signals of a SIP with more than 4 equiv of HMPA present. When separated ion pairs are formed they are easily recognized by the very characteristic lithium and phosphorus NMR signals of Li(HMPA)₃⁺ and Li(HMPA)₄⁺. In addition to securely identifying the CIP to SIP transition and hence information about the strength of the C-Li interaction, such experiments provide information about the aggregation state and the presence of chelating interactions.^[26] NMR studies of this type have been applied to sulfur and silicon substituted alkyl lithium reagents,^[26, 27, 28, 29, 30] aryllithium reagents,^[25, 27, 31] lithium phosphide,^[20] lithium sulfide,^[25] lithium selenolate,^[20] lithium stannate,^[24] lithium halides,^[25] lithium amides,^[32] lithium phenoxides,^[33] and metalated nitriles.^[34]

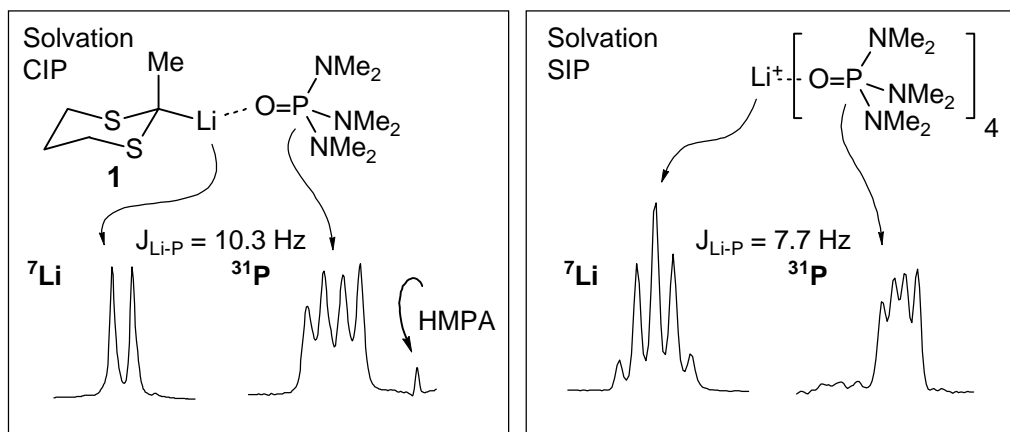


Figure 2. ^7Li and ^{31}P NMR spectra of a CIP and a SIP in 3:2 THF/ether at $-130\text{ }^\circ\text{C}$.

A typical HMPA titration (compound **2**) is shown in Fig. 3. In this example separated ions first appear at 1.0 equiv of HMPA. The signals are marked S^3 in Fig. 3 (1:3:3:1 quartet at -0.4 ppm in the ^7Li and 1:1:1:1 quartet at 27.15 ppm in the ^{31}P NMR spectra). By 3.0 equiv. of HMPA, ion separation is complete. The relative amounts of CIP and SIP in such spectra can be quantitated by integration or line-shape simulation, and the information used in the analysis of reaction mechanisms.

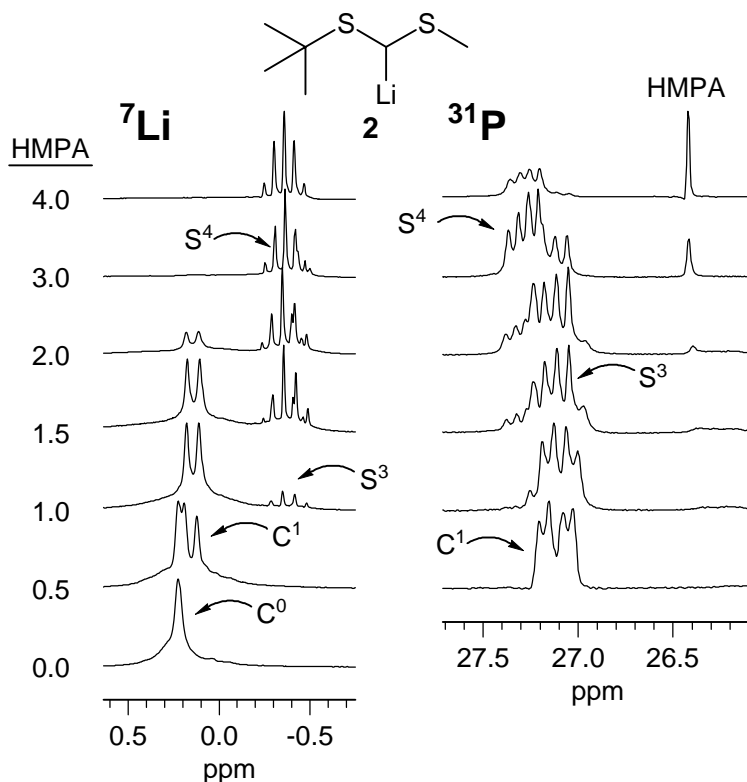


Figure 3. HMPA titration of 0.16 M *t*-butylthio(methylthio)methylithium (**2**) in 3:2 THF/ether at $-119\text{ }^\circ\text{C}$ ($\text{C} = \text{CIP}$, $\text{S} = \text{SIP}$, $\text{C}^1 = \text{R-Li}(\text{HMPA})_1$, $\text{S}^3 = \text{R}^- // \text{Li}(\text{HMPA})_3^+$, $\text{S}^4 = \text{R}^- // \text{Li}(\text{HMPA})_4^+$).

Fig. 4 provides a qualitative measure of the ease of ion-pair separation on treatment with HMPA of a few of the many systems we have examined. Highly localized anions such as simple alkyl and aryllithium reagents (**3-5**), lithium acetylides (**6**) and lithium alkoxides (**7**) do not undergo detectable dissociation to ion pairs even with many equivalents of HMPA. Highly delocalized lithium reagents, on the other hand, such as lithium fluorene (**8**) and trityllithium are already nearly fully ion-separated in THF, as are most alkylithium reagents bearing three good carbanion stabilizing groups such as Ph, PhS,

PhSe, PhTe and R_3Si (e.g **9**). Lithium reagents having two such groups are generally CIPs in THF. However, one or a few equivalents of HMPA is usually sufficient to cause partial or complete conversion to SIPs. An exception is bis(3,5-bistrifluoromethylphenylthio)methyl lithium (**10**), for which the strong electron withdrawal by the CF_3 groups results in 80% SIP in 3:2 THF/ether at $-78^\circ C$.

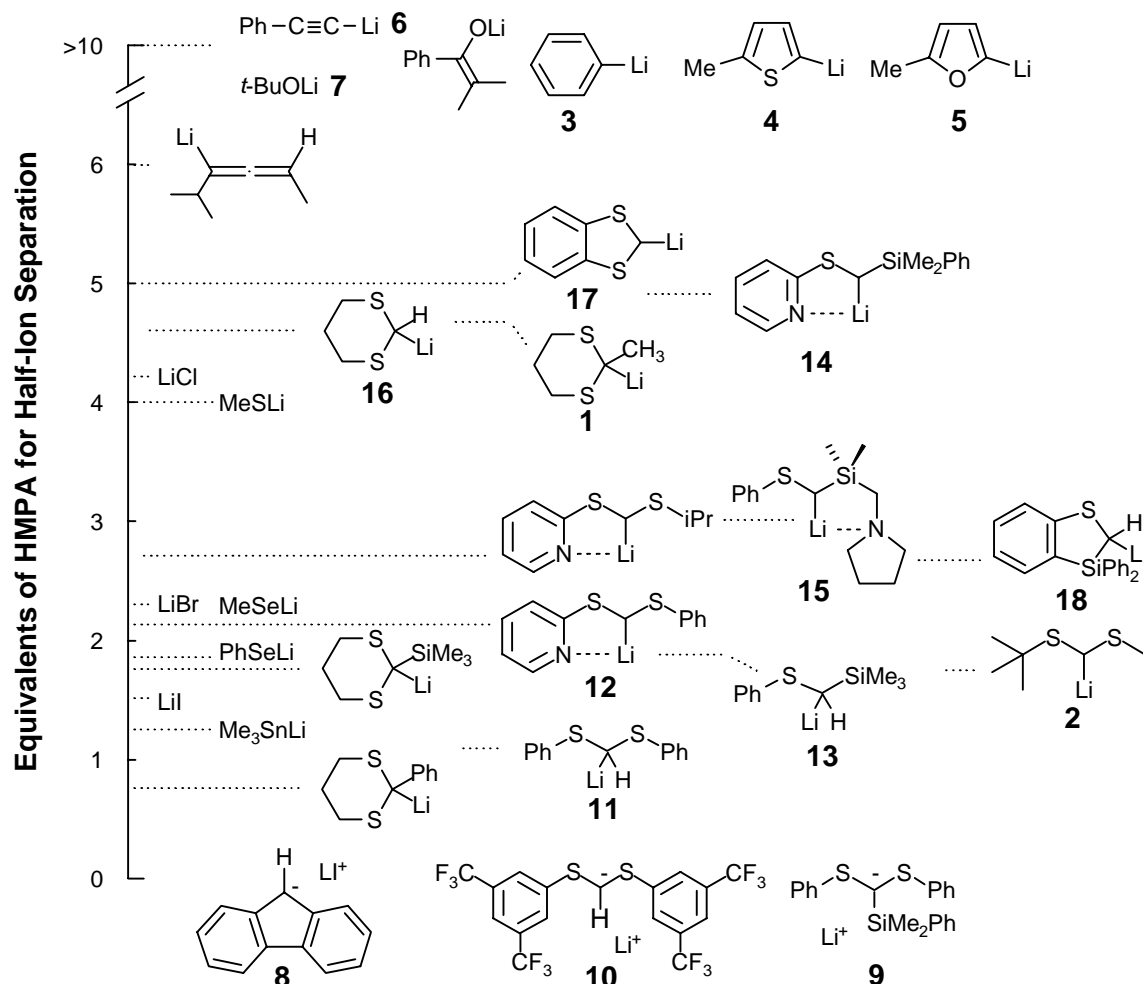
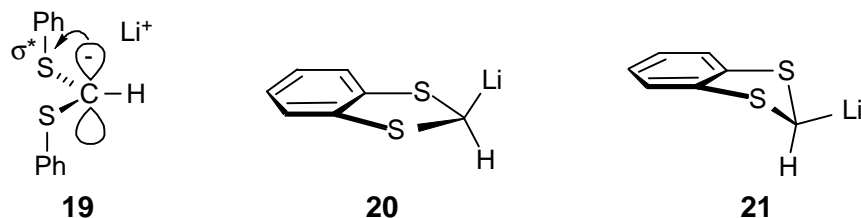


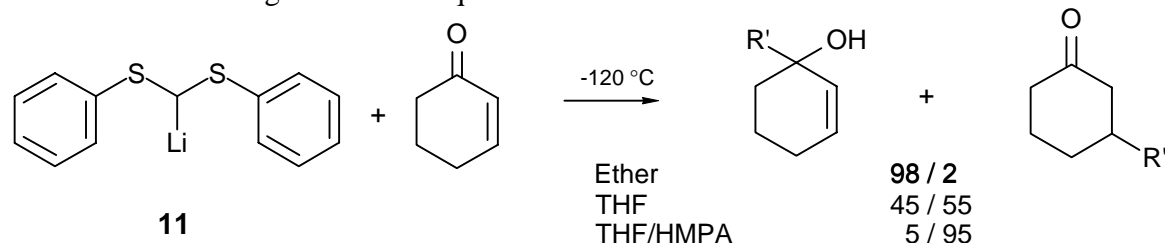
Figure 4. Relative ease of ion pair separation for representative lithium reagents in THF or 3:2 THF/ether at -120 to $-140^\circ C$.

The presence of potential chelating groups generally results in significantly more resistance to ion separation. Thus replacement of a phenylthio with an *o*-pyridylthio group results in a substantial increase in the concentration of HMPA required to cause significant ion separation (compare **11**, and **12**; **13** and **14**). Similarly, the chelating pyrrolidino methyl substituent in **15** requires more than an additional equivalent of HMPA for half ion-separation compared to the non-chelated model **13**. This can be viewed as direct evidence that such groups are, in fact, strongly chelated even in THF solution.

Another feature that has emerged from our studies is that constraining the anion-stabilizing groups in a ring as in dithianyllithiums and related structures generally results in more difficult ion-pair separation (compare **2** and **16**; **11** and **17**; **13** and **18** in Fig. 4). This effect can be ascribed to the fact that such groups cannot easily achieve the optimum $n-\sigma^*$ overlap required for effective charge delocalization.^[35,36] In acyclic systems, substituents tend to align themselves with the lone pair orbital or the C-Li bond to maximize stabilization (**19**). In cyclic systems such as **20** such alignment is only partially effective even if the system adopts a strained conformation such as **21**.^[29] Hence, there is more charge localization and a stronger C-Li bond.



1,2- vs 1,4-Addition to Enones. The effect of HMPA in favoring 1,4- over 1,2-addition of some types of lithium reagents under conditions of *kinetic* control was first reported in 1977. The proposal was made that this change was a consequence of conversion from CIP to SIP structures. [37, 38, 39, 40]



Several computational studies have found cyclic 4-membered transition states for the addition of Li-X species to carbonyl groups.^[41, 42, 43] Such cyclic transition states cannot operate for 1,4-additions to cyclic enones. However, once ion separation by solvent coordination is accomplished, 1,4-addition can occur smoothly to form the invariably more stable 1,4-adduct (Fig. 5). This hypothesis was supported by some evidence (for example, lower temperatures, which generally favor SIPs over CIPs, also favor 1,4-addition)^[39] but more detailed consideration was hampered by a lack of information about the ion pair status of almost all lithium reagents.

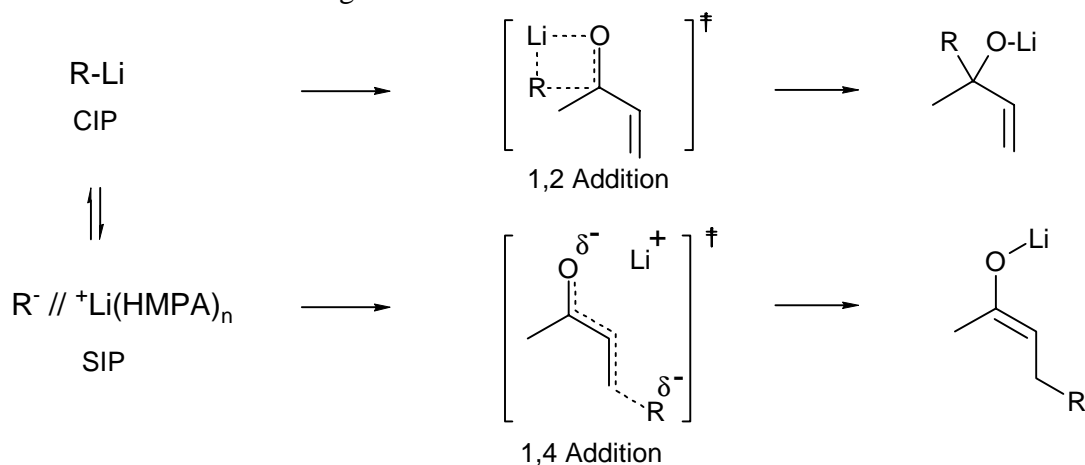


Figure 5. Mechanistic hypothesis for the regioselectivity of lithium reagent additions to enones.

We have been able to address this issue more directly with the HMPA-titration NMR technique since it allows determination of the fraction of SIP present in such solutions. A direct correlation between 1,4-addition and the fraction of SIP was not found (for example, 2-lithio-1,3-dithiane **16** gives >70% 1,4-addition with 1 equiv of HMPA present, even though <5% of SIP was present).^[37, 38] Thus the Curtin-Hammett principle applies – the barrier to interconversion of CIP and SIP is evidently lower than the barrier to reaction of R-Li with the enone. However, in a number of cases there was a close correlation between the ease of ion pair separation and fraction of 1,4-addition (Fig. 6), providing significant support for the hypothesis of Fig. 5. This cannot be the only effect, however, since with some lithium reagents (e.g. **10**) the fraction of 1,4-addition continued to increase even after conversion to SIP was complete. The addition of HMPA has two main effects. One is to increase the fraction of SIP, but a second and in some cases even more important effect is to strongly complex the lithium cation and hence reduce its ability to act as a Lewis acid to catalyze carbonyl addition and other reactions. Thus, we have suggested that the propensity for the SIP to partition between 1,2- and 1,4-addition is

strongly affected by the complexation of lithium to the carbonyl group, with the enone-lithium complex giving more 1,2-addition than the free enone.^[37, 38]

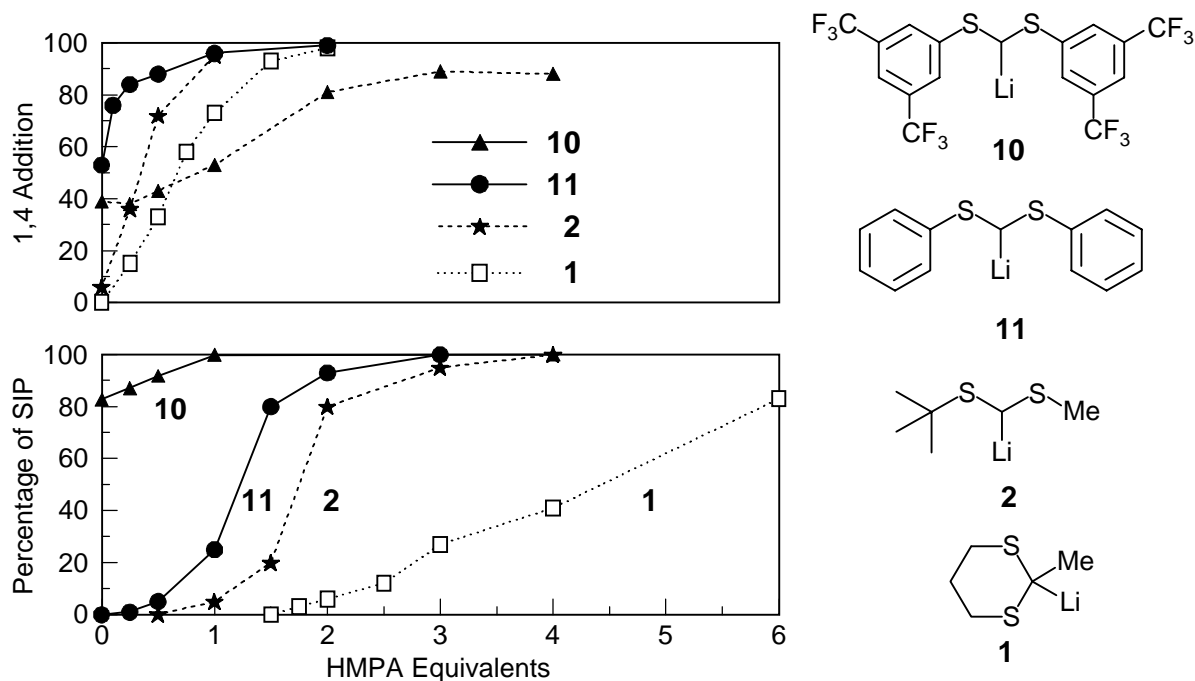


Figure 6. Fraction of 1,4-addition to cyclohexenone (top graph) and fraction of SIP in 3:2 THF/ether at $-120\text{ }^{\circ}\text{C}$ for lithium reagents **1**, **2**, **10**, and **11**.

S_N2 Reactions of Organolithium Reagents. The success of using lithium reagents for S_N2 substitutions varies widely, depending strongly on reaction conditions, structure of RLi and structure of the S_N2 substrate. For many lithium reagents conversion to organocuprates is required before successful alkylations can be performed.^[44] One possible origin of this diverse behavior arises from the “product separated ion” problem that arises when a CIP reacts in an S_N2 substitution — the lithium cation cannot easily follow the negative charge developing in the leaving group (Fig. 7). This effect can be recognized in gas phase S_N2 substitutions,^[45] and has been well documented in computational studies of such reactions.^[46, 47, 48, 49]

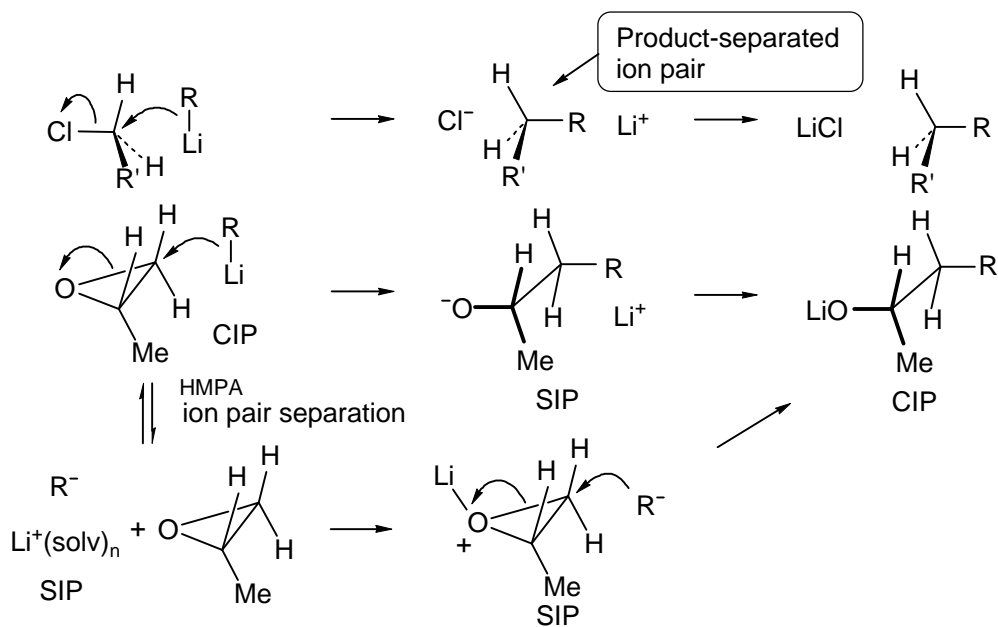


Figure 7. Contact and separated ion pairs in S_N2 substitutions.

Alkylations and epoxide openings seem to be particularly successful when performed with stabilized lithium reagents, such as metalated dithianes, and frequently in the presence of polar cosolvents such as DMPU or HMPA.^[50] This suggests that one way to avoid the “product separated ion” problem is to convert the CIP to an SIP, which has the beneficial effects of 1) providing a more charged and less encumbered carbanionic nucleophile and 2) allowing the lithium cation to assist departure of the leaving group.

We have performed a kinetic study of the alkylations of primary halides, epoxides and aziridines with lithiated sulfides such as 1,3-dithiane (**16**) and bis(arylthio)methylolithiums **10** and **11**. Some interesting observations that relate to the CIP/SIP issue are presented in Fig. 8, which shows the rate acceleration caused by the addition of HMPA for the alkylation of three lithium reagents with BuI (for **10**) and BuCl (for **11** and **16**). Compound **10** is essentially a fully SIP in THF (see Fig. 6), and shows essentially no rate increase on addition of HMPA. Compound **11** is an easily separated CIP, and increases in rate by a factor of 400. Lithiodithiane **16**, on the other hand, is a strong CIP which requires several equivalents of HMPA for significant development of SIP. It increases in rate by a factor of at least 60,000,000 upon addition of >10 equiv of HMPA. This and other evidence suggest strongly that most or all of the alkylation occurs through the SIP, and that these rate increases correspond directly to the fractional increase in SIP with higher HMPA concentrations. These rate ratios are also minimum estimates of the difference in reactivity of CIP and SIP lithium reagents.

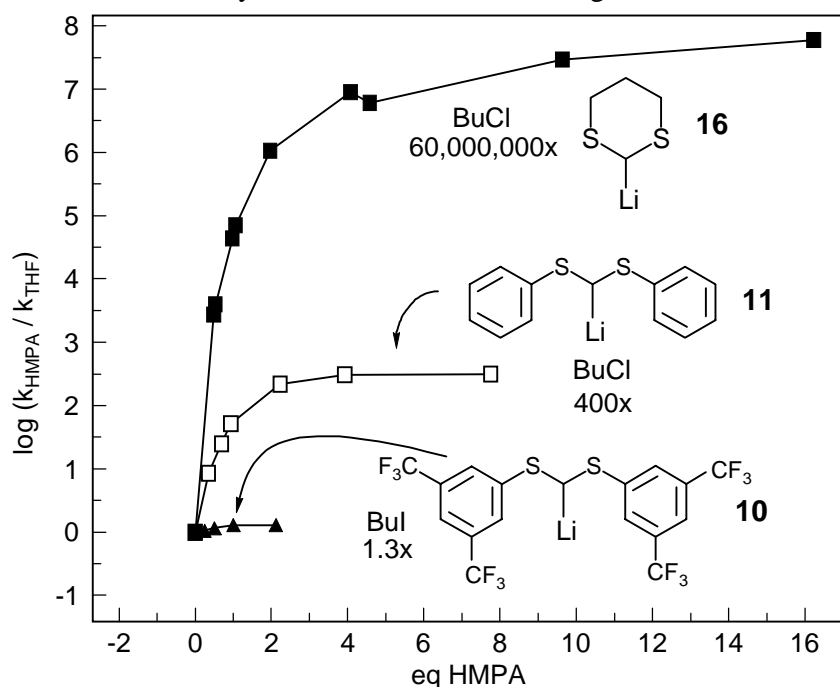


Figure 8. Relative rates of alkylation (ratio of second order rate constants) of three lithium reagents with butyl halides in THF at -78 °C as a function of equivalents of HMPA.

Summary.

The conversion of lithium reagent contact ion pairs (CIP) to separated ion pairs (SIP) results in large changes in reactivity and selectivity. We have described an NMR technique which allows determination of this ion pair behavior in the presence of HMPA. In favorable cases, this method allows quantitation of the fraction of SIP present. This information has provided insights into the effects of solvents on the 1,2- to 1,4-addition ratio of organolithium reagents, as well as the widely divergent rate effects caused by HMPA when lithium reagents are used as nucleophiles in S_N2 substitutions.

Experimental.

NMR Experiments. All multinuclear NMR experiments were performed in 10 mm NMR tubes using a wide-bore AM-360 spectrometer at 139.962 MHz (^7Li). The digital resolution was 0.51 Hz. For a typical 0.15 M solution, excellent signal to noise ratios were obtained after 32 transients.

***t*-Butylthio(methylthio)methane.** To a dried, N_2 -purged, 50 mL round bottom flask with stir bar, which was fitted with a septum and maintained under positive N_2 pressure, was added 26.8 mL (39.9 mmol) of 1.49 M MeLi in Et_2O . The solution was cooled to -78°C and *t*-butyl mercaptan (3.6 g, 39.9 mmol) was added dropwise followed by 3.86 g (40.0 mmol) of $\text{CH}_3\text{SCH}_2\text{Cl}$. The cold bath was removed, and the solution was allowed to warm to room temperature and stir for 3 h. The contents were transferred to a separatory funnel, 25 mL of hexane was added, and the solution was washed with 3 x 30 mL of 10% NaOH, 30 mL of H_2O , and 30 mL of brine and dried over anhydrous MgSO_4 . The solvents were removed by rotary evaporation, and the product was fractionally distilled (110°C at 50 mm Hg) to yield 1.77 g (11.8 mmol, 29.4%) of a colorless liquid. Density = 0.9580 g / mL. ^1H NMR (300 MHz, CDCl_3): δ 1.37 (CH_3 , s, 9H), 2.21 (CH_3 , s, 3H), 3.68 (CH_2 , s, 2H). ^{13}C NMR (75.4 MHz, CDCl_3): δ 15.20 (SCH_3), 30.81 (CH_3), 33.87 (CH_2), 43.27 (C). The spectroscopic results agree with literature data.^[51]

HMPA Titration of *t*-Butylthio(methylthio)methylithium (2). To a dried, N_2 -purged, 10 mm NMR tube fitted with a septum and maintained under positive N_2 pressure were added 78.4 μL (75.1 mg, 0.500 mmol) of *t*-butylthio(methylthio)methane, 1.8 mL of THF, and 1.2 mL of Et_2O . The NMR tube was cooled to -78°C and 0.32 mL (0.506 mmol) of 1.58 M *t*-BuLi in pentane was added. The NMR tube was warmed to -20°C until the characteristic bright yellow color of *t*-BuLi in THF had dissipated (approximately 5 min.). A series of ^7Li and ^{31}P NMR spectra at -119°C were taken during an HMPA titration (1 equiv. of HMPA = 87.0 μL). The spectra are shown in Fig. 3.

Procedures for rate studies: A stock solution of the lithium reagent was prepared; **16** will be used as an example. To a oven-dried 25 mL round bottom flask containing a magnetic stir bar was added 1.226 g (10.20 mmol) of freshly recrystallized 1,3-dithiane. The flask was sealed with a septum, purged with N_2 . 60 μL (0.23 mmol) of tetradecane was weighed in, and the flask charged with 16.0 mL of THF. The solution was cooled to -78°C and 4.0 mL (10.2 mmol) of 2.55 M *n*-BuLi was added and the flask allowed to warm to -20°C in a freezer for 2 h. The stock solution was used for no more than two sets of kinetics.

To five labeled (1,2,3,4, and Q), oven-dried, N_2 purged, long-neck, 5 mL round bottom flasks containing magnetic stir bars, was weighed in 20 μL (0.088 mmol) of dodecane, and 3.0 mL of THF. At this time HMPA or other additives were weighed into flasks 1-4 in appropriate amounts. The flasks were cooled to -78°C in a dry ice/acetone bath. To flask Q was added 100 μL (1.60 mmol) of MeI. All flasks were then charged with 0.50 mL of the stock solution of **16**. The kinetics were carried out by injecting 1.00 mmol of the substrate (butyl halide or propylene oxide) into flasks 1-4. After the specified time each flask was quenched with 100 μL of MeI (to quantitate remaining RLi), followed 5 min later by 0.1 mL of saturated NH_4Cl solution.

The flasks were warmed to room temperature and the septa removed. To each flask was added ~3 mL of hexanes, and enough MgSO_4 or Na_2SO_4 to dry it. The samples were immediately analyzed by GC without further purification.

The concentration of tetradecane, RH and RLi in the RLi stock solution was determined from the flask labeled Q by dividing the amount of tetradecane, protonated, and methylated products respectively by the total volume of liquid in flask Q during the reaction. The initial concentration of RLi in flasks 1-4 was determined by subtracting the amount of protonated product in the stock solution from the total of all products in the numbered flask. Flasks which contained more than 30% protonation were not used for analysis. The initial concentration of substrate was calculated from the amount of substrate added divided by the total volume. The final concentrations of RLi and substrate were calculated by subtracting the amount of product from the initial amounts and again dividing by the total volume. The equivalents of additives were calculated by dividing the concentration of RLi by the concentration of the

additive. To insure that no product catalysis was taking place all reactions were carried out under initial rate conditions, and only rarely were points at greater than 10% reaction used. The second order rate constant was calculated using the formula:

$$k_2 t = 1 / ([RLi]_0 - [Substrate]_0) \ln ([substrate]_0 [RLi]_F / [RLi]_0 [substrate]_F)$$

To insure that the correct amount of stock solution had been added, the ratio of tetradecane:dodecane was determined from the volume of stock solution and the weighed amount of dodecane, and compared with the GC trace. Points were discarded if the ratios differed by more than 5%. A mass balance percentage was also determined by adding the amounts of substrate, methylated, and protonated product and dividing by the original amount of RH weighed into the flask. If the mass balance was below 80% the point was discarded.

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