A ^{1}H and ^{13}C NMR Study of the Structure of Sulfur-Stabilized Lithiated Allylic Carbanions

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(Received May 10, 1995)

NMR studies of the solution structures of lithiated (*E*)-1-(*t*-butylthio)but-2-ene (**4**) and lithiated (*E*)-1-(phenylthio)but-2-ene (**6**) are reported. The structure of lithiated (*E*)-1-(*t*-butylthio)but-2-ene (**4**) is best described as a transoid carbanion with the allylic carbons C1, C2, and C3 having intermediate sp^2–sp^3 hybridization. In (**4**) the heteroatom and non-allylic substituent do not play any significant role in carbanion stabilization. Lithiated (*E*)-1-(phenylthio)but-2-ene (**6**) differs from (**4**) in that it exhibits *cis* geometry about the C1–C2 bond and the phenylthio group participates in helping to stabilize allylic charge. There is a discrepancy between the geometry about the C1–C2 bond in the solution and solid structures of (**4**) in the presence of TMEDA.

The lithiated carbanion of allylic sulfides[1)] are widely used, synthetically important reagents. They are highly nucleophilic and their reactions with alkylating agents, carbonyl compounds and other electrophiles are rapid, high yielding and easily executed.[2—5)] Lithiated allylic sulfides have been used routinely in synthetic work.[6,7)]

There is little information available on the solution structure of lithiated allylic sulfides. NMR studies of the structure of phosphorus-stabilized[8)] and sulfone-stabilized[9)] allylic anions provide some insight into the bonding, configuration, and hybridization of the individual atoms in the allyl moiety. A low temperature X-ray crystal structure of lithiated (*E*)-1-(*t*-butylthio)but-2-ene (**4**) complexed with TMEDA provides data on the structure of a sulfur-stabilized allyl anion in the solid state.[10)] The crystal structure of (**4**) in the presents of TMEDA clearly shows the non-allylic group and the sulfur atom adopting a cisoid configuration with the allylic backbone, with the lithium cation being trihapto bound to C1, C2, and C3 of the allylic backbone.

It was of interest to us to establish if the anion of (*E*)-1-(*t*-butylthio)but-2-ene (**4**) maintained its structure in solution, thus enabling a satisfactory ground state solution structure to be proposed for these synthetically important reagents. This paper examines the solution structure of lithiated (*E*)-1-(*t*-butylthio)but-2-ene (**4**) and lithiated (*E*)-1-(phenylthio)but-2-ene (**6**) by using a combination of ^{1}H and ^{13}C NMR techniques.

Results and Discussion

Preparation of Allylic Substrates and Their Corresponding Organolithium Reagents. The synthetic procedures are summarized in Scheme 1. (*E*)-1-(*t*-Butylthio)but-2-ene (**3**) and (*E*)-1-(phenylthio)but-2-ene (**5**) were easily prepared in high geometric purity from a crotonaldehyde precursor. Reduction of crotonaldehyde with lithium aluminium hydride gave the (*E*)-allylic alcohol (**1**) which was converted to the (*E*)-allylic bromide (**2**) with phosphorus tribromide. To minimize isomerization the (*E*)-allylic bromide (**2**) was immediately converted to compounds (**3**) (45% overall yield) and (**5**) (56% overall yield). Analytical GC of the distilled products (**3**) and (**5**) indicated an *E*/*Z* ratio of 93/7. Metallation of the (*E*)-allylic substrates (**3**) and (**5**) using 1.1 equiv of *t*-butyllithium in THF at −50 °C afforded the anions (**4**) and (**6**) respectively.

The cyclic allylic sulfide, 2*H*-5,6-dihydrothiopyran (**9**), was synthesized from the commercially available tetrahydrothiopyran-4-one (Scheme 1). The ketone was reduced to the corresponding alcohol (**7**) with sodium borohydride in ethanol, then converted to its mesylate (**8**) with methanesulfonyl chloride in the presence of triethylamine and a catalytic amount of 4-dimethylaminopyridine (DMAP) at −30 °C. Elimination in the presence of 1,5-diazobicyclo[4.3.0]non-5-ene (DBN) and heat gave the required cyclic allylic sulfide (**9**) in an overall yield of 63%. The lithiated cyclic anion (**10**) was formed by treating the substrate (**9**) with 1.1 equiv of *t*-butyllithium at −50 °C in THF.

^{1}H and ^{13}C NMR Study of Sulfur-Stabilized

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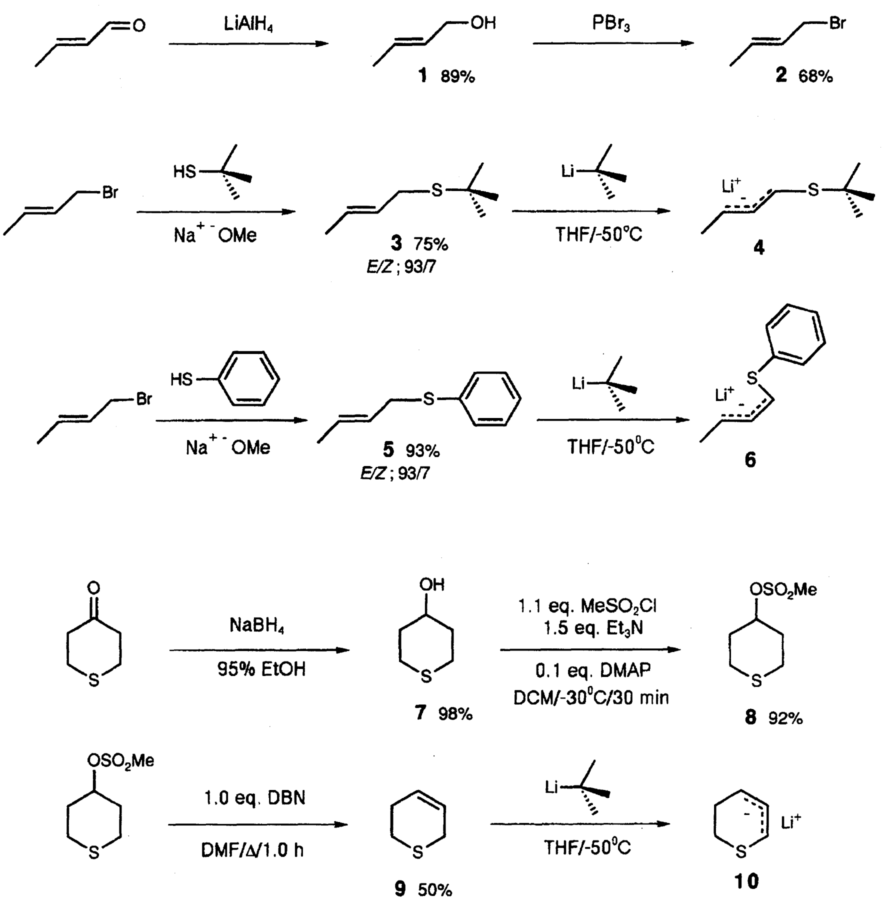


Scheme 1.

Allylic Carbanions. ^{1}H and ^{13}C NMR spectroscopy has previously been extensively used to characterize the structure of carbanions in homogeneous solutions.[8,9,11—15] Several structural features of sulfur-stabilized allylic carbanions are well suited for study by NMR spectroscopy through the interpretation of the ^{1}H and ^{13}C chemical shifts, proton–proton ($^{3}J_{\mathrm{H,H}}$) couplings and carbon–proton ($^{1}J_{\mathrm{C,H}}$) couplings.

This paper discusses a qualitative analysis of changes in chemical shift and spin–spin coupling constants which allows a number of empirical relationships concerning the type of bonding, hybridization state, electron density, and overall geometry of sulfur-stabilized allylic carbanions to be drawn. Such a study of chemical shifts and spin–spin coupling constants allows a successful model for these allylic systems to be constructed. An appreciation of the changes which occur in chemical shift and spin–spin coupling constants can be obtained by comparing the values for these parameters in the carbanion with those in the substrate.

Protons attached to electron rich carbons experience an upfield shift relative to the corresponding protons in the neutral precursor due to an increase in electron density at the attached carbon. The upfield chemical shift, due to increasing electron density in ^{1}H NMR spectroscopy, may be complicated by the anisotropy of the carbanions π-system and additional upfield or compensating downfield changes may be observed in forming the carbanion from the precursor. The interpretation of the changes in the chemical shifts of the carbanion can be further complicated by electron delocalization onto the sulfur atom. Similarly, upfield ^{13}C chemical shift changes occur forming the carbanion from the precursor but the changes are much larger and less sensitive to effects other than changes in electron density. Thus, for the allylic carbanions studied, qualitative discussion of the ^{1}H and ^{13}C chemical shifts of nuclei in these anions can be used to describe differences in electron density within these carbanions.

Interpretation of changes in spin–spin coupling constants ($^{1}J_{\mathrm{C,H}}$) and ($^{3}J_{\mathrm{H,H}}$) in charged species may be complicated by the large number of variables which make up the $^{1}J_{\mathrm{C,H}}$ and $^{3}J_{\mathrm{H,H}}$ parameters.[16] Analysis of changes which occur in the spin–spin coupling constants from substrate to carbanion can be interpreted in terms of changes in hybridization of the allylic carbon skeleton ($\Delta^{1}J_{\mathrm{C,H}}$), changes in configuration within the allylic system ($\Delta^{3}J_{\mathrm{H,H}}$), and an indication of the changes in the type of bonding between allylic carbon nuclei ($\Delta^{3}J_{\mathrm{H,H}}$ and $\Delta\delta$).

^{1}H and ^{13}C NMR spectra of a carbanion precursor and the carbanion formed on deprotonation, qualitatively reflect a number of important features. In general:[12,13] (i) When a carbanion is formed from an

sp^3-hybridized carbon an increase in $^1J_{C,H}$ can be related to an increase in sp^2-hybrid character of the carbon and a decrease of $^1J_{C,H}$ implies a charge increase. (ii) A decrease in $^1J_{C,H}$ for a carbon which was originally sp^2-hybridized can be related to an increase in sp^3 hybrid character of the carbon. (iii) A decrease in the chemical shift (shielding) of any carbon atom reflects an increase in the charge density at that carbon. An increase in chemical shift (deshielding) reflects a decrease in charge density. (iv) Changes in proton chemical shifts can be interpreted following similar reasoning as in (iii), with the proton shielding or deshielding being a second order effect. (v) Changes in $^3J_{H,H}$ reflect changes in the ability of protons to sense one another, which can be used as a guide to changes in bonding between the vicinal protons and changes in the relative configuration of these protons.

To facilitate the discussion of sulfur-stabilized allylic carbanions, Table 1 draws together the ^{1}H and ^{13}C NMR data for the (*E*)-1-(*t*-butylthio)but-2-ene and (*E*)-1-(phenylthio)but-2-ene systems.

^{1}H NMR of the Carbanions of (*E*)-1-(*t*-Butylthio)but-2-ene (4) and (*E*)-1-(Phenylthio)but-2-ene (6). The most pronounced chemical shift changes in forming the carbanion from the neutral precursor occur for the protons attached to the allylic backbone, H1 (−0.54 and −1.09 ppm), H2 (+0.51 and +0.37 ppm), and H3 (−1.60 and −1.36 ppm). These changes in chemical shift can be visualized by directly comparing the substrate proton spectrum to the spectrum of the carbanion (Fig. 1) for the (*E*)-1-(*t*-butylthio)but-2-ene system. The changes for the methyl protons H4 (−0.07

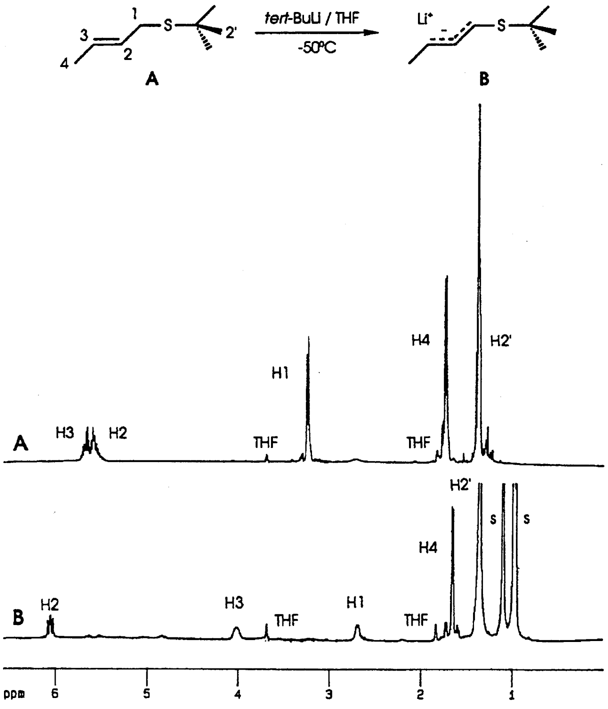
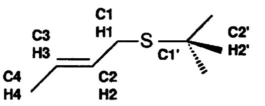
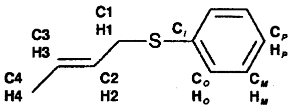


Fig. 1. ^{1}H NMR spectrum (400.14 MHz) illustrating the changes in proton chemical shift between (**A**) the neutral substrate (**3**) (at 300 K) and (**B**) the ground state carbanion of (*E*)-1-(*t*-butylthio)but-2-ene (**4**) (at 220 K), s=solvent peaks.

Table 1. ^{1}H and ^{13}C NMR Difference Data for the (*E*)-1-(*t*-Butylthio)but-2-ene and (*E*)-1-(Phenylthio)but-2-ene Systems





Nuclei	Δδ (ppm) ($\delta_C-\delta_S$)	$\Delta^3J_{H,H}$ (Hz) ($^3J_C-^3J_S$)	Nuclei	Δδ (ppm) ($\delta_C-\delta_S$)	$\Delta^3J_{H,H}$ (Hz) ($^3J_C-^3J_S$)
H1	−0.54	4.9	H1	−1.09	1.1
H2	0.51	$^3J_{1,2}3.2$ & $^3J_{2.3}-1.0$	H2	0.37	$^3J_{1,2}0.5$ & $^3J_{2,3}-1.2$
H3	−1.60	−0.7 & −0.3	H3	−1.36	−1.2 & −0.2
H4	−0.07	0.1	H4	−0.05	1.0
H2′	−0.27	—	H_{ortho}	−0.20	−0.2
			H_{meta}	−0.26	−0.2
			H_{para}	−0.42	−0.2

Nuclei	Δδ (ppm) ($\delta_C-\delta_S$)	$\Delta^1J_{C,H}$ (Hz) ($^1J_C-^1J_S$)	Nuclei	Δδ (ppm) ($\delta_C-\delta_S$)	$\Delta^1J_{C,H}$ (Hz) ($^1J_C-^1J_S$)
C1	3.2	4.4	C1	−6.9	3.2
C2	23.0	−15.4	C2	16.3	−21.1
C3	−42.8	−9.5	C3	−37.5	−5.1
C4	1.9	−3.8	C4	1.8	−3.5
C1′	2.5	—	C_{ipso}	14.9	—
C2′	−0.7	−2.4	C_{ortho}	−1.9	−4.9
			C_{meta}	−5.4	−1.9
			C_{para}	−5.3	−5.0

and −0.05 ppm), the non-allylic *t*-butyl protons H2′ (−0.27 ppm) and the phenyl protons H_o, H_m, and H_p (−0.20 to −0.42 ppm depending on their location on the ring) are small in comparison.

The smaller changes in chemical shifts can be ascribed to a number of secondary effects brought about by the proximity of the electron rich allylic system and changes in the stabilizing characteristics of the sulfur atom due to a dispersal of the negative charge away from the allylic system and onto the non-allylic substituents via the vacant d-orbitals of the sulfur,[14,17] or amongst other effects, $n \rightarrow \sigma^*$ delocalization (negative hyperconjugation) into the $S\text{–}C_{\text{non-allylic}}$ bond.[18]

The more dramatic changes of chemical shift for H1, H2, and H3 can be interpreted in terms of an increase in electron density at C1 and C3, and a decrease in electron density at C2.[8,9,15,19] The largest change in chemical shift, H3 can be rationalized as follows. In the precursor the protons H2 and H3 are attached to sp^2-hybridized carbon nuclei and are therefore deshielded compared with the H1 protons which are attached to an sp^3-hybridized carbon. In the carbanion, the delocalization of charge perturbs the allylic double bond system, which removes some of the deshielding associated with the π-electrons in the double bond. The delocalization would effectively increase the charge density at C1 and C3.

The net effect of a localization of charge density onto C3 as reflected in the chemical shift change of H3 is more dramatic than that experienced by the proton at C1 by virtue of the initial deshielding of the proton at C3 in the precursor. This delocalization of electrons over the allylic system may be indicative of changes in the bond order between carbons C1–C2 and C2–C3 and the hybridization state of the carbons C1, C2, and C3.

$^3J_{\text{H,H}}$ in the Carbanions of (*E*)-1-(*t*-Butylthio)but-2-ene (4) and (*E*)-1-(Phenylthio)but-2-ene (6). On formation of the carbanion, the change in $^3J_{\text{H,H}}$ coupling constants in the allylic sulfides are the most pronounced for the $^3J_{1,2}$ couplings between H1 and H2 (increase 1.1 and 4.9 Hz), with a significant but smaller change in $^3J_{2,3}$ couplings between H2 and H3 (decrease 0.7 and 1.2 Hz) (Table 1). The large change of the $^3J_{1,2}$ coupling can be attributed to an increase in electron delocalization between C1–C2 in the carbanion as compared with the neutral precursor, that is, a delocalization of charge across the allylic system. Additionally, a more favorable electronic pathway (i. e. $^3J_{1,2}$ with H1 and H2 *trans* is typically larger than $^3J_{1,2}$ with H1 and H2 *cis*) may be the reason for this coupling change. The small decrease of $^3J_{2,3}$ indicates a decrease in the electronic pathway between these two nuclei, that is, a decrease in the π-bonding between C2 and C3. This is consistent with the partial delocalization of these π-electrons over the allylic carbon skeleton. It should be noted that the configuration about the C2–C3 bond remains intact in going from substrate to the initially formed carbanion (at 220 K), that is to say, deprotonation of *trans* allylic sulfide precursors gives *trans* allylic sulfide carbanions as the first formed carbanions.[20,21]

It is important to note that the $^3J_{\text{H,H}}$ vicinal coupling constant is a powerful tool for describing the configuration between two adjacent proton atoms. For neutral compounds, both *cis* and *trans* π-systems[22,23] and configurationally fixed σ-system[22d,24] geometries are elucidated routinely with this diagnostic tool. However, the use of ^3J coupling constants to describe the geometry in delocalized charged systems is not well documented in these types of carbanions.[9,25] Lithiated (*E*)-1-(phenylthio)but-2-ene has a $^3J_{1,2}=7.0$ Hz whilst lithiated (*E*)-1-(*t*-butylthio)but-2-ene has a $^3J_{1,2}=10.2$ Hz and it is not possible to unequivocally determine the geometry about the C1–C2 bond by first order methods.

There could be two distinct possibilities for the $^3J_{1,2}$ coupling constant of 10.2 Hz. Firstly, as with localized π-bonds, vicinal $^3J_{\text{H,H}}$ coupling constants have two distinct values, *trans* $^3J_{\text{H,H}}=12$—18 Hz, typically 17 Hz, and *cis* $^3J_{\text{H,H}}=6$—12 Hz, typically 10 Hz, as can be derived from the Karplus equation.[23,26,27] The individual magnitude of the *cis* and *trans* vicinal coupling would be a function of the bond order (i. e. the degree of delocalization) between the two carbon atoms in the delocalized system and considerably smaller to that found in a localized π-system. The $^3J_{1,2}$ coupling constant of 10.2 Hz is indicative of a *trans* configuration about the C1–C2 bond and a coupling constant of the order of 6 to 7 Hz would indicate a *cis* configuration in these delocalized anions. Or, alternatively, the intermediate value of 10.2 Hz indicates a time averaged $^3J_{1,2}$ for the *cis* and *trans* carbanions undergoing rapid rotation on the NMR timescale about the C1–C2 bond.

It was not possible to establish the geometry of H1 and H2 about the C1–C2 bond in either of the anions (**4**) or (**6**) by 1-D nuclear Overhauser enhancement (nOe) experiments.

$^3J_{\text{H,H}}$ in the Carbanion of 2*H*-5,6-Dihydrothiopyran. The *cis* constrained cyclic allylic precursor 2*H*-5,6-dihydrothiopyran (**9**) was synthesized (Scheme 1) and the carbanion (**10**) generated. The anion has a $^3J_{1,2}$ coupling constant of 5.7 Hz. The anion has fixed *cis* geometry about C1–C2 and although this value is lower than the expected value of 7.0 Hz found in the non-cyclic systems, it has been documented that in restricted ring systems, such as (**10**), the $^3J_{\text{H,H}}$ coupling constant decreases with ring size.[26] The $^3J_{1,2}$ *cis* coupling constant of 5.7 Hz will be larger in a noncyclic *cis* allylic carbanion and that $^3J_{1,2}$ coupling constant between 5.5 to 7.5 Hz would be expected for a noncyclic *cis* allylic carbanion. It follows that the carbanion of (*E*)-1-(phenylthio)but-2-ene, which exhibits a $^3J_{1,2}$ coupling of 7.0 Hz, has a *cis* relationship between the H1 and H2 protons about C1–C2, Fig. 2 (B) and (C). Coincidentally, this intermediate value for delocalized *cis* system compares well with localized *cis* σ-systems

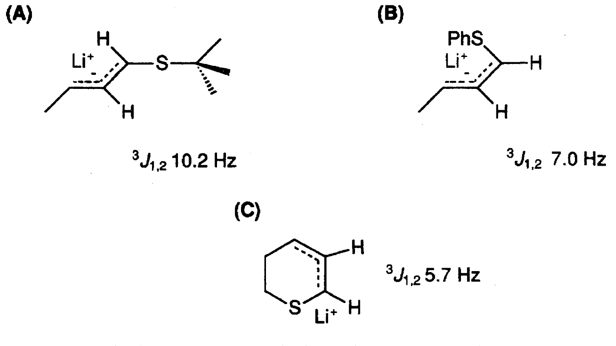


Fig. 2. (**A**) Lithiated (*E*)-1-(*t*-butylthio)but-2-ene (**4**) shows the characteristic $^3J_{1,2}$ coupling constant of 10.2 Hz and indicates *trans* geometry about the C1–C2 bond. (**B**) The carbanion of (*E*)-1-(phenylthio)but-2-ene, (**6**) shows a $^3J_{1,2}$ coupling constant of 7.0 Hz and indicates *cis* geometry for the protons about the C1–C2 bond. (**C**) 2*H*-5,6-Dihydrothiopyran lithiated anion (**10**) with fixed *cis* C1–C2 geometry has a coupling constant of 5.7 Hz for the H1 and H2 protons.

and *cis* π-systems.[22,23]

At all temperatures studied (175 to 298 K) only one species was observed and there was no evidence for the presences of more than one stereoisomer. A value of 18.24 kcal mol^{-1} [28] for the interconversion of cisoid and transoid sulfur-stabilized allylic carbanions has previously been calculated for an allylthio analogue (**11**) of the current systems and a rotational barrier for the interconversion of rotamers should have been encountered in this temperature range (Chart 1). Structural studies[11,29] of unstabilized allyllithium carbanions have indicated that the structure of the carbanions are fixed in one of the two possible geometries and that there is a significant barrier associated with the interconversion of these two rotamers. For allyllithium itself, the barrier is calculated to be 17.1 kcal mol^{-1} and is determined to be 10.7 kcal mol^{-1}.[29]

The pronounced chemical shift change of H1, H2, and H3 indicates that there is delocalization of charge across the carbanionic backbone with increased electron density at carbons C1 and C3. The delocalization of charge between C1–C2 clearly imposes a barrier to rotation about this bond. Thus, there is no free rotation about C1–C2 in the present case. The protons H1 and H2 in the carbanion of (*E*)-1-(*t*-butylthio)but-2-ene, (**4**) must adopt a *trans*-configuration about C1–C2, that is to say, the $^3J_{1,2}$ coupling constant of 10.2 Hz is indicative of *trans* geometry in delocalized carbanions of this type. This value for *trans* geometry in heteroatom-stabilized allylic carbanions compares well with the value 9.8—10.1 Hz coupling constant for *trans* geometry in the electronically related enolate sodiomalondialdehyde[30] and alkali metal β-dicarbonyl enolates (9.8—10.7 Hz).[31,32]

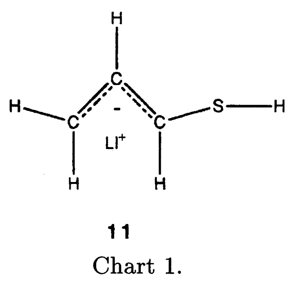


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Chart 1.

The preference for a *cis* relationship between protons about C1–C2 in the carbanion of (*E*)-1-(phenylthio)but-2-ene, (**6**) rather than with the *trans* relationship observed in lithiated (*E*)-1-(*t*-butylthio)but-2-ene (**4**), Fig. 2 (A) and (B), can be rationalized in terms of electronic and steric effects. For the C1–C2 transoid allylic carbanion, the *t*-butyl group together with the attached sulfur atom are *exo* or *anti* with respect to the allylic system. In this geometry the allylic or [$A^{(1,3)}$]-strain arising from the interaction between the *t*-butyl group with H3 destabilizes the *endo* isomer with respect to the *exo*. In the (*E*)-1-(phenylthio)but-2-ene case, the smaller phenyl group and the attached sulfur atom adopt an *endo* or *syn* orientation such that the group is *cis* to C2–C3. The stabilizing phenyl substituent may prefer to be *endo* when there are no steric interactions with groups attached to C3, due to electronic effects. It has been noted that the isoelectronic carbanions derived from *N*,*N*-dimethylhydrazones and related derivatives of ketones adopt analogous geometries.[33]

^{13}C NMR of the Carbanions of (*E*)-1-(*t*-Butylthio)but-2-ene (4) and (*E*)-1-(Phenylthio)but-2-ene (6). The model for allylic sulfide systems can be expanded by examining the ^{13}C data which provide a better indication of the changes which occur on the carbon backbone in these sulfur-stabilized allylic carbanions. As illustrated in Fig. 3, the most dramatic changes in chemical shift occur at C1 (+3.2 and −6.9 ppm), at C2 (+23.0 and +16.3 ppm), and at C3 (−42.8 and −37.5 ppm) (Table 1) of the allylic system. There are only small changes in chemical shift of the methyl carbons C4 (+1.9 and +1.8 ppm), the non-allylic carbons C1′ (+2.5 ppm), and C2′ (−0.7 ppm) of the *t*-butyl group. The *ipso* carbon of the aromatic ring shows a dramatic shift (+14.9 ppm) to lower field. The other aromatic carbons, C_{ortho} (−1.9 ppm), C_{meta} (−5.4 ppm), and C_{para} (−5.3 ppm) are also shifted to a lesser extent to higher field. The larger changes in the non-allylic phenyl group may be due to a partial stabilization of the charge on the allylic system via a delocalization pathway across the sulfur atom (pπ–dπ–pπ interaction)[14,15] and delocalization of this charge into the aromatic system. An associated shift to higher field for C1 is expected with an increase in the electron density, as a consequence of this delocalization via the vacant d-orbitals of the sulfur atom. Smaller changes in chemical shift of C2 and C3 in the phenyl allylic sulfide system compared with C2 and C3 in the *t*-butyl sulfide are due to a net decrease in charge of the allylic system in the phenyl sulfide case. The delocalization of allyl-

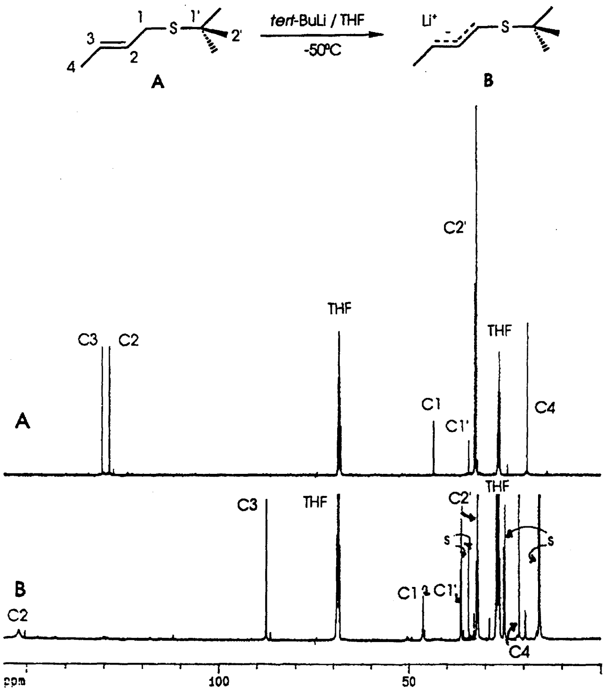


Fig. 3. ^{13}C NMR (100.62 MHz) of (*E*)-1-(*t*-Butylthio)-but-2-ene (**A**) Substrate (**3**) (at 300 K), and (**B**) Carbanion (**4**) (at 220 K), showing the dramatic chemical shifts of C1, C2, and C3 of the allylic system, s=solvent peaks.

ic charge across the allylic and phenyl system via the sulfur atom is also in agreement with the proton NMR data. The large variation of chemical shift of C2 and C3 is in full agreement with the associated changes of H2 and H3 reported earlier and can be interpreted as an increase in electron density at C3 and a decrease of electron density at carbon C2.

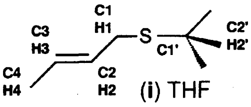
For an initially sp^3-hybridized carbon an increase in $^1J_{\mathrm{C,H}}$ can be related to a rehybridization of that carbon to a sp^2 hybridized carbon and a decrease in $^1J_{\mathrm{C,H}}$ implies a charge increase. For both the allylic sulfide carbanions examined the change in ^1J coupling for C1 is small (increase 3.2 and 4.4 Hz) which may be interpreted as the result of an interplay of charge delocalization with an associated decrease in sp^3 hybridization of C1 and charge localization at C1. The changes in the ^1J couplings for C2 (decrease 15.4 and 21.1 Hz) and C3 (decrease 5.1 and 9.5 Hz) indicate a change in the hybridization state of both nuclei which may be attributed to the partial delocalization of the π-electrons over the allylic carbon backbone. The degree of rehybridization was typically greater at C2 than at C3 but a full measure of this change in hybridization can only be appreciated by comparing such changes with those in other heteroatom-stabilized allylic carbanions.[34)]

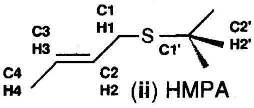
Formation of Carbanions in the Presence of TMEDA. Further examination of the solution structure of sulfur-stabilized allylic carbanions was conducted with investigation of structural changes which may occur on addition of a metal complexing agent. The investigation explored the influences that the metal complexing agents *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), hexamethyl phosphoric triamide (HMPA), and 1,1,4,7,7-pentamethyldiethylenetriamine (PMDTA), have on the lithium atom and this inherent effect on the bonding, electronic distribution, and geometry of the perturbed anions after complexation of the lithium cation. HMPA has a pronounced effect on the reactivity of allylic carbanions with electrophiles such as 4-*t*-butoxycyclopent-2-enone.[6,7a)] In such reactions, coordination of lithium is believed to be of pivotal importance, particularly when transition state arguments are sought to explain the dramatic diastereo- or regio- selectivity of the reaction.[6,7a,7b,36)]

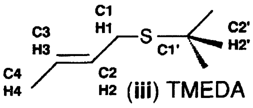
For the (*E*)-allylic *t*-butyl sulfide carbanion, the metal complexing agents TMEDA, PMDTA, and HMPA were used to functionally co-ordinate with the lithium cation. ^{1}H and ^{13}C NMR spectra were acquired and compared with the THF only anions and also the substrate to investigate changes which may have arisen in the structure of this anion. The effect of added metal complexing agents were in all instances seen as a changing of the resonance frequencies of both H1, C1 and H3, C3 nuclei to higher field as compared with the carbanion in neat THF (Table 2). The upfield shifts of C1 and C3 in the complexed carbanions probably reflect a slight increase in the electron density at these nuclei. The shifts to higher field for the TMEDA and PMDTA cases are of a similar magnitude to those experienced in the neat THF case, whilst HMPA shows a 25—30% increase in the shift to higher field for both C1 and C3 (Table 2).

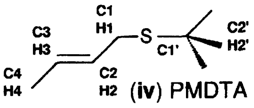
The mechanisms by which and the exact structure induced by metal complexing agents on anionic species is still a matter of conjecture.[36—38)] Suffice it to say that it has been well documented[2,36,37)] that the effect of HMPA is to strongly solvate the metal counter ion, inducing the formation of highly reactive monomers, ion pairs or free ions which produce charge redistribution or delocalization on the carbanion. In general, TMEDA and PMDTA complex with the lithium counter ion less strongly than HMPA and in doing so functionally co-ordinate with the counter ion in a contact ion pair (CIP) relationship with its anionic partner.[14,39)] The effects of stronger complexation by HMPA would be to release charge back onto the allylic framework of the carbanion through the breakdown of electrostatic interactions between carbanion and counter cation. In general for the TMEDA and PMDTA cases, full dissociation of electrostatic charge does not occur. Due to the slightly greater ability of the nitrogen atoms in the TMEDA and PMDTA to donate electrons to the solvent sphere of the lithium cation as compared to the solvent molecules (tetrahydrofuran), the overall effect will be to cause a small release of charge back onto the allylic backbone as complexation of the lithium cation with TMEDA or

Table 2. ^{1}H and ^{13}C NMR difference data for the (*E*)-1-(*t*-butylthio)but-2-ene in (i) neat THF, (ii) the presence of HMPA, (iii) TMEDA, and (iv) with PMDTA.









Nuclei	$\Delta\delta$ (ppm) ($\delta_C-\delta_S$)	$\Delta^3J_{H,H}$(Hz) ($^3J_C-^3J_S$)	Nuclei	$\Delta\delta$ (ppm) ($\delta_C-\delta_S$)	$\Delta^3J_{H,H}$(Hz) ($^3J_C-^3J_S$)	Nuclei	$\Delta\delta$ (ppm) ($\delta_C-\delta_S$)	$\Delta^3J_{H,H}$(Hz) ($^3J_C-^3J_S$)	Nuclei	$\Delta\delta$ (ppm) ($\delta_C-\delta_S$)	$\Delta^3J_{H,H}$(Hz) ($^3J_C-^3J_S$)
H1	−0.54	4.9	H1	−0.72	4.0	H1	−0.56	4.9	H1	−0.50	5.0
H2	0.51	$^3J_{1,2}$3.2 & $^3J_{2,3}-1.0$	H2	0.47	$^3J_{1,2}$4.3 & $^3J_{2,3}-3.2$	H2	0.52	$^3J_{1,2}$3.7 & $^3J_{2,3}-1.1$	H2	0.64	$^3J_{1,2}$4.4 & $^3J_{2,3}-1.5$
H3	−1.60	−0.7 & −0.3	H3	−2.44	−2.5 & −0.3	H3	−1.63	−1.2 & −0.5	H3	−1.75	−2.9 & 0.4
H4	−0.07	0.1	H4	−0.14	0.6	H4	−0.06	0.0	H4	0.02	0.2
H2′	−0.27	—	H2′	−0.25	—	H2′	−0.26	—	H2′	−0.27	—

Nuclei	$\Delta\delta$ (ppm) ($\delta_C-\delta_S$)	$\Delta^1J_{C,H}$(Hz) ($^1J_C-^1J_S$)	Nuclei	$\Delta\delta$ (ppm) ($\delta_C-\delta_S$)	$\Delta^1J_{C,H}$(Hz) ($^1J_C-^1J_S$)
C1	3.2	4.4	C1	−3.3	11.0
C2	23.0	−15.4	C2	24.9	−15.2
C3	−42.8	−9.5	C3	−57.5	−10.6
C4	1.9	−3.8	C4	−1.8	−3.8
C1′	2.5	—	C1	0.8	—
C2′	−0.7	−2.4	C2′	−0.1	−2.4

PMDTA takes place.

The downfield shift of the H2 and C2 nuclei in the HMPA complexed carbanion is marginally greater than that of the carbanion in neat THF, with the H2 and C2 nuclei of the TMEDA and PMDTA carbanions shifting downfield by a similar amount to that of the carbanion in the absence of metal complexing agents. The smaller change in H2 and C2 chemical shift of the carbanion in the presence of HMPA may indicate the type of association between the lithium and the anion in the absence of HMPA. If the lithium counter ion were trihapto bound to the allylic carbanion backbone, as determined by X-ray crystallography,[10)] an increase in chemical shift of H2 and C2 on disruption of the contact ion pair by a strong metal complexing agent, such as HMPA, is expected. The change in chemical shift of H2 and C2 are much smaller than that of H1, C1 and H3, C3 in the carbanion in the presence of HMPA and this suggest that the electrostatic interaction between anion and cation in the (*E*)-allylic *t*-butyl sulfide carbanion in neat THF is weaker at C2 compared to the stronger interactions at C1 and C3 (dihapto bonding). Alternatively, these changes can be interpreted as a weak interaction with C2 and a strong interaction (monohapto bonding) with either C1 or C3. Trihapto bonding of the lithium to the allylic backbone clearly does not occur in solution. Previously reported data[19)] on isotopically perturbed allyllithium anion is in agreement with a rapidly equilibrating monohapto model.

Increases in the $^3J_{2,3}$ coupling and the $^1J_{C,H}$ coupling at C1 in the carbanion in the presence of HMPA (Table 2, (ii)) clearly indicate delocalization of the increased charge at C3 across the C2–C3 bond and an increase in the sp^2-character at C1 compared to the carbanion in neat THF. The changes in the coupling constants and chemical shifts of the allylic nuclei indicate the association of the lithium with the anion changes from a CIP to a strongly solvated ion pair on addition of HMPA. The changes in the $^3J_{2,3}$ coupling and the $^1J_{C,H}$ coupling at C1 in the TMEDA and PMDTA complexed anions are much smaller than in the case where HMPA is the complexing agent. The minimal changes in coupling constant and insignificant change in the chemical shift of the allylic nuclei of the TMEDA and PMDTA complexed anions compared with the anions in neat THF indicate that these anions are still in a CIP arrangement with the cation.

The anions of lithiated (*E*)-1-(*t*-butylthio)but-2-ene in the presence of TMEDA, PMDTA, and HMPA all exhibit a $^3J_{1,2}$ coupling constant in the range 10.5±1.0 Hz and this clearly indicates *trans* geometry about the C1–C2 bond. Clearly there is a disparity between the structure of lithiated (*E*)-1-(*t*-butylthio)but-2-ene in the presence of TMEDA obtained from X-ray crystallography[10)] to that observed in solution.

Regardless of a possible explanation for these structural differences in the TMEDA complexed lithiated (*E*)-1-(*t*-butylthio)but-2-ene system, it can be stated from the results obtained in this study that there are dramatic differences in the solution and solid structure of these highly charged nucleophilic species. Conclusions with regard to the solution structure of carbanions and other reactive species based on the results of X-ray crystallography may therefore not be valid.

A more rigorous study which further addresses the association that the lithium counter cation has with its anionic allylic partner is currently in preparation and will be presented elsewhere.

Experimental

General. Infrared spectra were recorded on a Digilab FTS 20/80 Fourier Transform spectrometer from the solid samples within potassium bromide discs. Ultraviolet spectra were recorded on a Hitachi 150-20 spectrometer with ethanol as the solvent. Electron impact mass spectra were recorded on an AEI MS9 spectrometer at 70 eV. Melting points were recorded on a Reichert melting point stage and are uncorrected. ^{1}H NMR (400.14 MHz), and ^{13}C NMR (100.62 MHz) spectra were recorded on Bruker WM 400 and AMX 400 spectrometers fitted with a multinuclear probe with deuterated tetrahydrofuran (THF-d_8) as the sample solvent for carbanion and substrate data acquisition. The spectrometer was locked on the high field THF-d_8 signal and spectra acquired were referenced to the low field THF-d_8 signal in ^{1}H NMR (δ=3.70) and ^{13}C NMR (δ=68.6). Routine ^{1}H NMR and ^{13}C NMR were recorded on a Bruker AC-200 (200 and 50 MHz) spectrometer as dilute solution (5—12% w/v) in deuterated chloroform $CDCl_3$ with tetramethylsilane (1%). The spectra acquisition temperatures stated have an error of ±5 K and were obtained from the uncalibrated spectrometer variable temperature unit.

Starting reagents were obtained from Merck or Aldrich. THF-d_8 was distilled prior to use. *t*-Butyllithium as a solution in pentane was standardized by titration against 2,5-dimethoxybenzyl alcohol according to the method of Winkle, Lansinger, and Ronald.[40] Hexamethylphosphoric triamide (HMPA) was stirred with calcium hydride under nitrogen for 36 h, then distilled at reduced pressure and stored over 4 Å molecular sieves. *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine (TMEDA) and 1,1,4,7,7-pentamethyldiethylenetriamine (PMDTA) were distilled under reduced pressure prior to use.[41]

Preparation of (*E*)-But-2-en-1-ol (1). A solution of crotonaldehyde (48.0 g, 0.68 mol) in dry diethyl ether (100 ml) was added slowly to a stirred suspension of lithium aluminium hydride (9.0 g, 0.24 mol) in dry diethyl ether (300 ml), under nitrogen, which had been refluxed for 1 h prior to addition. The resultant mixture was stirred for 24 h at room temperature to produce a grey cloudy suspension which was refluxed gently for 1 h prior to work up. The mixture was quenched with a saturated sodium sulfate solution and filtered through celite to give a pale yellow solution which was dried (Na_2SO_4). Evaporation of the solvent at atmospheric pressure left the crude product (46.4 g, 94%) which was distilled to give (*E*)-but-2-en-1-ol as a colorless liquid (43.9 g, 89%), bp 42—44 °C/30—40 mmHg [lit,[42] bp 121.2 °C (752 mmHg, 1 mmHg=133.322 Pa)].

Preparation of (*E*)-1-Bromobut-2-ene (2). (*E*)-But-2-en-1-ol (18.8 g, 0.26 mol) in dry diethyl ether (100 ml) at 0 °C under nitrogen was treated dropwise with freshly distilled phosphorus tribromide (35.2 g, 0.13 mol, 12.4 ml) in dry diethyl ether (75 ml). The reaction mixture was then stirred for a further 3 h with cooling (10 to 12 °C) before being poured into ice water (200 ml). The organic phase was washed consecutively with water, saturated potassium carbonate solution and brine, and then dried (Na_2SO_4). The ether was removed by distillation at atmospheric pressure to give the crude product as a brownish liquid with an acute smell (23.9 g, 68%). The crude (*E*)-1-bromobut-2-ene was used without further purification, as distillation at 97—99 °C/760 mmHg [lit,[42] bp 97—99 °C/760 mmHg], resulted in some isomerization of the (*E*)-isomer as established by GC analysis.

Preparation of (*E*)-1-(*t*-Butylthio)but-2-ene (3). Sodium 1,1-dimethylethane thiolate was prepared by treating sodium methoxide [from sodium (2.4 g, 104 mg-atoms) in methanol (90 ml)] with 1,1-dimethylethane thiol (7.7 g, 85 mmol, 9.7 ml) at 0 °C under nitrogen. After 15 min, (*E*)-1-bromobut-2-ene (12.1 g, 89.7 mmol) was added dropwise as a neat solution. The resultant solution was stirred at 0 °C for 3 h and then poured into ice water (100 ml) and extracted with ether (2×100 ml). The combined ether extracts were washed consecutively with saturated potassium carbonate solution and brine, and dried (Na_2SO_4). Evaporation of the solvent left a pale yellow oil (11.9 g, 92%) which was distilled to give (*E*)-1-(*t*-butylthio)but-2-ene as a clear liquid (9.5 g, 73%), bp 110 °C/40 mmHg (Kugelrohr) [lit,[43] bp 83—85 °C/20—30 mmHg], ^{1}H NMR (400 MHz) (298 K) (THF-d_8) δ=1.40 (s, 9×H2′), 1.75 (dd, $^3J_{3,4}$=6.1 Hz, $^4J_{2,4}$=0.9 Hz, 3×H4), 3.26 (d, $^3J_{1,2}$=5.3 Hz, 2×H1), 5.58 (dtq, $^3J_{1,2}$=7.0 Hz, $^3J_{2,3}$=15.2 Hz, $^4J_{2,4}$=1.2 Hz, H2), and 5.68 (dq, $^3J_{2,3}$=14.9 Hz, $^3J_{3,4}$=6.5 Hz, H3). ^{13}C NMR (100 MHz) (298 K) (THF-d_8) δ=19.1 (qdd, ^1J=126.8 Hz, ^2J=5.7 Hz, ^3J=5.7 Hz, C4), 32.6 (q of sept, ^1J=127.4 Hz, ^3J=4.5 Hz, 3×C2′), 32.9 (tdd, ^1J=138.3 Hz, ^2J=5.7 Hz, ^3J=5.7 Hz, C1), 43.7 (s of m, C1′), 128.7 (dtd, ^1J=153.4 Hz, ^2J=6.7 and 6.7 Hz, C2), and 130.6 (ddq, ^1J=156.5 Hz, ^2J=6.7 and 6.7 Hz, C3). GC[44] analysis of the distilled products (Superox 0.1 fused silica capillary column, SGE, N_{eff} 78500, 50 m×0.33 mm i.d., column temperature 80 °C, column head pressure 90 kPa) indicated (*E*)- and (*Z*)-isomers in the ratio, 93 : 7 and the presence of a regioisomer (3-(*t*-butylthio)but-1-ene) accounting for 3% of the total yield.

Preparation of Lithiated (*E*)-1-(*t*-Butylthio)but-2-ene (4). Preparation was carried out with the use of standard Schlenk techniques under an atmosphere of high-purity argon in 5 mm high resolution NMR tubes. To a solution of (*E*)-1-(*t*-butylthio)but-2-ene (30 mg, 0.21 mmol) in freshly distilled THF-d_8 (0.20 ml) at −50 °C was slowly added *t*-butyllithium (134 μl, 1.7 M, 1.1 equiv). Immediately upon deprotonation of the substrate the color of the initially clear solution changed to deep yellow in color and the following NMR spectra were recorded, ^{1}H NMR spectrum (400 MHz) (250 K) (THF-d_8) δ=1.13 (s, 9×H2′), 1.68 (dd, $^3J_{3,4}$=6.2 Hz, $^4J_{2,4}$=1.2 Hz, 3×H4), 2.72 (d, $^3J_{1,2}$=10.2 Hz, H1), 4.08 (dq, $^3J_{2,3}$=14.2 Hz, $^3J_{3,4}$=6.2 Hz, H3), and 6.09 (ddq, $^3J_{1,2}$=10.2 Hz, $^3J_{2,3}$=14.2 Hz, $^4J_{2,4}$=1.2 Hz, H2). ^{13}C NMR spectrum (100 MHz) (220 K) (THF-d_8) δ=21.0, qddd, ^1J=123.0 Hz, ^2J=7.0 Hz, ^3J=7.0 Hz, ^4J=4.3 Hz, C4), 31.9 (q of sept, ^1J=125.0 Hz, ^3J=4.2 Hz, 3×C2′), 36.1 (d of m, ^1J=142.7 Hz, C1), 46.2 (s of m, C1′), 87.8 (ddq, ^1J=147.0 Hz, ^2J=6.1 and 6.1 Hz, C3), and 151.7 (d of m, ^1J=138.0 Hz, C2).

Preparation of (a) Lithiated (*E*)-1-(*t*-Butylthio)-but-2-ene/TMEDA, (b) Lithiated (*E*)-1-(*t*-Butylthio)but-2-ene/HMPA, (c) Lithiated (*E*)-1-(*t*-Butylthio)but-2-ene/PMDTA. Preparation was carried out with the use of standard Schlenk techniques under an atmosphere of high-purity argon in 5 mm high resolution NMR tubes. To a solution of (*E*)-1-(*t*-butylthio)but-2-ene (30 mg, 0.21 mmol) in freshly distilled THF-d_8 (0.20 ml) at 0 °C was added 2.2 equivalents of a metal complexing agent, TMEDA or HMPA or PMDTA. The solution was lowered to −50 °C and *t*-butyllithium (134 µl, 1.7 M, 1.1 equiv) added to give a yellow solution and the following NMR spectra were recorded.

(**a**) ^{1}H NMR spectrum (400 MHz) (220 K) (THF-d_8) δ= 1.14 (s, 9×H2′), 1.69 (d, $^{3}J_{3,4}$=6.1 Hz, H4), 2.70 (d, $^{3}J_{1,2}$= 10.2 Hz, H1), 4.05 (dq, $^{3}J_{2,3}$=13.7 Hz, $^{3}J_{3,4}$=6.0 Hz, H3), and 6.10 (dd, $^{3}J_{1,2}$=10.7 Hz, $^{3}J_{2,3}$=14.1 Hz, H2).

(**b**) ^{1}H NMR spectrum (400 MHz) (220 K) (THF-d_8) δ=1.15 (s, 9×H2′), 1.61 (d, $^{3}J_{3,4}$=6.7 Hz, 3×H4), 2.54 (d, $^{3}J_{1,2}$=9.3 Hz, H1), 3.24 (dq, $^{3}J_{2,3}$=12.4 Hz, $^{3}J_{3,4}$=6.2 Hz, H3), and 6.05 (dd, $J_{1,2}$=11.3 Hz, $^{3}J_{2,3}$=12.0 Hz, H2). ^{13}C NMR spectrum (100 MHz) (220 K) (THF-d_8) δ=17.3 (q of m, ^{1}J=123.0 Hz, C4), 29.6 (d of m, ^{1}J=149.3 Hz, C1), 32.5 (q of m, ^{1}J=125.0 Hz, 3×C2′), 44.5 (s of m, C1′), 73.1 (ddq, ^{1}J=145.9 Hz, ^{2}J=6.3 and 2.6 Hz, C3), and 153.6 (ddd, ^{1}J=138.2 Hz, ^{2}J=5.7 and 2.6 Hz, C2).

(**c**) ^{1}H NMR spectrum (400 MHz) (220 K) (THF-d_8) δ= 1.13 (s, 9×H2′), 1.77 (d, $^{3}J_{3,4}$=6.3 Hz, 3×H4), 2.76 (d, $^{3}J_{1,2}$=10.3 Hz, H1), 3.93 (dq, $^{3}J_{2,3}$=12.0 Hz, $^{3}J_{3,4}$=6.9 Hz, H3), and 6.22 (dd, $^{3}J_{1,2}$=11.4 Hz, $^{3}J_{2,3}$=13.7 Hz, H2). ^{13}C NMR spectrum (100 MHz) (220 K) (THF-d_8) δ=21.3 (qdd, ^{1}J=122.9 Hz, ^{2}J=7.8 Hz, ^{3}J=7.8 Hz, C4), 31.7 (q of m, ^{1}J=124.2 Hz, 3×C2′), 37.0 (d of m, ^{1}J=145.9 Hz, C1), 45.9 (s of m, C1′), 83.6 (d of m, ^{1}J=144.8 Hz, C3), and 151.7 (d of m, ^{1}J=140.1 Hz, C2).

Preparation of (*E*)-1-(Phenylthio)but-2-ene (5). (*E*)-1-Bromobut-2-ene (2.9 g, 21.5 mmol) was added dropwise to sodium phenylthiolate, prepared from sodium methoxide [from sodium (0.58 g, 25.2 mg-atoms) in methanol (25 ml)] and benzenethiol (2.3 g, 21 mmol, 2.1 ml) at 0 °C under nitrogen. The resultant solution was stirred at 0 °C for 4 h and then poured into ice water (50 ml) and extracted with ether (2×50 ml). The combined ether extracts were washed consecutively with saturated potassium carbonate solution and brine, and dried (Na_2SO_4). Evaporation of the solvent left a dark yellow oil which was distilled to give (*E*)-1-(phenylthio)but-2-ene as a light yellow oil (3.3 g, 93%), bp 165 °C/30 mmHg (Kugelrohr) [lit,[45] bp 63—64 °C/0.5 mmHg], ^{1}H NMR spectrum (400 MHz) (298 K) (THF-d_8) δ=1.73 (d, $^{3}J_{3,4}$=5.6 Hz, 3×H4), 3.62 (d, $^{3}J_{1,2}$=5.6 Hz, 2×H1), 5.63 (dt, $^{3}J_{1,2}$=7.0 Hz, $^{3}J_{2,3}$=15.1 Hz, H2), 5.66 (dq, $^{3}J_{2,3}$= 15.1 Hz, $^{3}J_{3,4}$=6.6 Hz, H3), 7.23 (t, $^{3}J_{meta,para}$=7.5 Hz, H_{para}), 7.34 (dd, $^{3}J_{ortho,meta}$=7.5 Hz, $^{3}J_{meta,para}$=7.5 Hz, 2×H_{meta}), and 7.41 (d, $^{3}J_{ortho,meta}$=7.5 Hz, 2×H_{ortho}). ^{13}C NMR spectrum (100 MHz) (298 K) (THF-d_8) δ=19.0 (qdd, ^{1}J=126.8 Hz, ^{2}J=5.7 Hz, ^{3}J=5.7 Hz, C4), 37.9 (tdd, ^{1}J=141.4 Hz, ^{2}J=5.7 Hz, ^{3}J=5.3 Hz, C1), 127.7 (ddd, ^{1}J=162.1 Hz, ^{2}J=7.5 Hz, ^{3}J=7.5 Hz, C_{para}), 128.7 (dtd, ^{1}J=157.4 Hz, ^{2}J=6.5 and 1.6 Hz, C2), 130.3 (dq, ^{1}J=153.3 Hz, ^{2}J=6.6 Hz, C3), 130.6 (dd, ^{1}J=162.1 Hz, ^{2}J=7.9 Hz, 2×C_{ortho}), 131.4 (ddd, ^{1}J=162.1 Hz, ^{2}J=7.4 and 7.4 Hz, 2×C_{meta}), and 139.1 (s of m, C_{ipso}). GC analysis of the distilled products (Superox 0.1 fused-silica capillary column, SGE, 50 m×0.33 mm i.d., column temperature 150 °C, column head pressure 110 kPa) revealed (*E*)- and (*Z*)-isomers in the ratio 93 : 7 and the presence of a regioisomer (3-(phenylthio)but-1-ene) accounting for 4% of the total yield.

Preparation of Lithiated (*E*)-1-(Phenylthio)but-2-ene (6). Preparation was carried out with the use of standard Schlenk techniques under an atmosphere of high-purity argon in 5 mm high resolution NMR tubes. To a solution of (*E*)-1-(phenylthio)but-2-ene (30 mg, 0.18 mmol) in freshly distilled THF-d_8 (0.20 ml) at −50 °C was slowly added *t*-butyllithium (118 µl, 1.7 M, 1.1 equiv). Immediately upon deprotonation of the substrate the color of the initially clear solution changed to deep yellow in color and the following NMR spectra were recorded, ^{1}H NMR spectrum (400 MHz) (220 K) (THF-d_8) δ=1.68 (d, $^{3}J_{3,4}$=6.6 Hz, 3×H4), 2.53 (d, $^{3}J_{1,2}$=6.7 Hz, H1), 4.30 (dq, $^{3}J_{2,3}$=13.9 Hz, $^{3}J_{3,4}$=6.4 Hz, H3), 6.00 (dd, $^{3}J_{1,2}$=7.5 Hz, $^{3}J_{2,3}$=13.9 Hz, H2), 6.81 (t, $^{3}J_{meta,para}$=7.3 Hz, H_{para}), 7.08 (dd, $^{3}J_{ortho,meta}$=7.3 Hz, $^{3}J_{meta,para}$=7.3 Hz, 2×H_{meta}), and 7.21 (d, $^{3}J_{ortho,meta}$= 7.3 Hz, 2×H_{ortho}). ^{13}C NMR spectrum (100 MHz) (220 K) (THF-d_8) δ=20.8 (qdd, ^{1}J=123.3 Hz, ^{2}J=6.9 Hz, ^{3}J=6.9 Hz, C4), 31.0 (ddd, ^{1}J=144.5 Hz, ^{2}J=8.9 Hz, ^{3}J=2.9 Hz, C1), 92.8 (ddq, ^{1}J=148.2 Hz, ^{2}J=5.8 and 5.8 Hz, C3), 122.4 (ddd, ^{1}J=157.1 Hz, ^{2}J=7.1 Hz, ^{3}J=7.1 Hz, C_{para}), 126.0 (ddd, ^{1}J=160.2 Hz, ^{2}J=6.7 and 6.7 Hz, 2×C_{meta}), 128.7 (d, ^{1}J=157.2 Hz, 2×C_{ortho}), 145.0 (d of m, ^{1}J=136.3 Hz, C2), and 154.0 (s, C_{ipso}).

Preparation of Tetrahydrothiopyran-4-ol (7). Tetrahydrothiopyran-4-one[46] (2.0 g, 17.2 mmol) in ethanol (4 ml, 95%) was reduced with sodium borohydride (0.34 g, 9.0 mmol) in ethanol (10 ml, 95%). The hydride was added over a period of 2 h at room temperature and the resulting mixture was heated at reflux for 4 h. The cooled mixture was neutralized with dilute hydrochloric acid and the resulting mixture was dried (K_2CO_3) and distilled. Tetrahydrothiopyran-4-ol (2.0 g, 98%), bp 80 °C/1.2 mmHg (Kugelrohr) [lit,[47] bp 84—85 °C/1.8 mmHg, mp 49 °C] was obtained as a liquid which solidified in the receiver.

Preparation of Tetrahydrothiopyran-4-yl Methanesulfonate (8). Freshly distilled methanesulfonyl chloride (0.32 g, 2.8 mmol, 216 µl) was added dropwise to a solution of freshly distilled triethylamine (0.36 g, 3.6 mmol, 0.5 ml), 4-(dimethylaminopyridine) (DMAP) (62 mg) and tetrahydrothiopyran-4-ol (0.30 g, 2.5 mmol) in dry dichloromethane (25 ml) at −30 °C. The reaction mixture was stirred for 30 min at −30 °C before being quenched with saturated sodium hydrogencarbonate solution (40 ml). The products were extracted with dichloromethane (2×20 ml), washed with water (2×40 ml) and brine (2×40 ml), and dried over anhydrous sodium sulfate. After removal of the solvent under reduced pressure, tetrahydrothiopyran-4-yl methanesulfonate (0.45 g, 92%) was obtained as a cream colored solid with a distinct odor. (Found: *m*/*z* 196.0242.) Calcd for $C_6H_{12}O_3S_2$: M^+, 196.0288). IR ν_{max} 3415brw, 2932m, 1431m, 1350s, 1171s, 1055w, 961m, 929s, and 846m cm^{-1}. UV λ_{max} (ethanol) 205 (ε, 1904) nm. ^{1}H NMR spectrum (200 MHz) (300 K) ($CDCl_3$) δ=1.95 to 2.22 (m, 8×Hring), 2.96 (s, CH_3), and 4.73 (dddd, $^{3}J_{3\alpha,4}$=6.7 Hz, $^{3}J_{4,5\alpha}$=6.7 Hz, $^{3}J_{3\beta,4}$=4.6 Hz, $^{3}J_{4,5\beta}$=4.6 Hz, CH). ^{13}C NMR spectrum (50 MHz) (300 K) ($CDCl_3$) δ=25.4 and 26.6 (C3 and C5), 33.7 (CH_3), 36.3 and 39.0 (C2 and C6), and 78.6 (C4). Mass spectrum: (electron impact) *m*/*z* 196 (M^+, 29%), 118 (58), 100 (100), 85 (81), 72 (42), 67 (44), and 45 (38).

Preparation of 2*H*-5,6-Dihydrothiopyran (9). A stirred solution of tetrahydrothiopyran-4-yl methanesulfonate (0.40 g, 2.0 mmol) and 1,5-diazobicyclo[4.3.0]non-5-ene (DBN) (0.25 g, 2.0 mmol, 0.25 ml) in dry *N*,*N*-dimethyl formamide (25 ml) was refluxed for 1.5 h. The reaction mixture was quenched with dilute hydrochloric acid (50 ml, 1.0 M, 1 M=1 mol dm^{-3}) and extracted into ether (1×100 ml, 2×50 ml). The ether layer was further washed with dilute hydrochloric acid (2×50 ml), then brine, and dried (Na_2SO_4). The ether was removed under reduced pressure to give the crude olefin (0.12 g, 60%) which was purified by flash chromatography (5% ethyl acetate/light petroleum) to give a clear liquid(0.10 g, 50%) with an acute smell. The 2*H*-5,6-dihydrothiopyran was further purified by distillation, bp 100 °C/70 mmHg (Kugelrohr) [lit,[47b)] bp 75 °C/58 mmHg], ^{1}H NMR spectrum (400 MHz) (300 K) (THF-d_8) δ=2.36 (dtd of m, $^3J_{4,5}$=3.6 Hz, $^3J_{5,6}$=2.1 Hz, $^4J_{3,5}$=0.6 Hz, 2×H5), 2.78 (t, $^3J_{5,6}$=5.8 Hz, 2×H6), 3.17 (dd of m, $^3J_{2,3}$=3.6 Hz, $^4J_{2,4}$=1.6 Hz, 2×H2), 5.86 (ddddd, $^3J_{3,4}$=10.7 Hz, $^3J_{4,5\alpha}$=3.5 Hz, $^3J_{4,5\beta}$=3.5 Hz, $^4J_{2\alpha,4}\equiv{}^4J_{4,6\alpha}$=1.6 Hz, $^4J_{2\beta,4}\equiv{}^4J_{4,6\beta}$=1.6 Hz, H4), and 5.92 (ddddd, $^3J_{2\alpha,3}$=3.4 Hz, $J_{2\beta,3}$=3.4 Hz, $^3J_{3,4}$=10.7 Hz, $^4J_{3,5\alpha}$=1.7 Hz, $^4J_{3,5\beta}$=1.7 Hz, H3). ^{13}C NMR spectrum (100 MHz) (300 K) (THF-d_8) δ=26.9 (t of m, ^1J=135.3 Hz, C5), 27.7 (tdd, ^1J=126.7 Hz, ^2J=4.3 and 1.7 Hz, C6), 39.2 (tdd, ^1J=131.8 Hz, ^2J=5.0 Hz, ^3J=2.0 Hz, C2), 126.1 (ddt, ^1J=158.8 Hz, ^2J=11.8 and 6.2 Hz, C3), and 129.6 (ddt, ^1J=157.9 Hz, ^2J=10.3 and 5.6 Hz, C4).

Preparation of Lithiated 2*H*-5,6-Dihydrothiopyran (10). Preparation was carried out with the use of standard Schlenk techniques under an atmosphere of high-purity argon in 5 mm high resolution NMR tubes. *t*-Butyllithium (193 μl, 1.7 M, 1.1 equiv) was slowly added to a solution of 2*H*-5,6-dihydrothiopyran (30 mg, 0.30 mmol) in freshly distilled THF-d_8 (0.20 ml) at −50 °C. Immediately upon deprotonation of the substrate the color of the initially clear solution changed to red in color and the following NMR spectra were recorded, ^{1}H NMR spectrum (400 MHz) (220 K) (THF-d_8) δ=1.77 (d, $^3J_{2,3}$=5.7 Hz, H2), 2.25 (m, 2×H6), 2.50 (m, 2×H5), 4.05 (dt, $^3J_{3,4}$=9.6 Hz, $^3J_{4,5}$=4.0 Hz, H4), and 6.33 (dd, $^3J_{2,3}$=3.1 Hz, $^3J_{3,4}$=9.6 Hz, H3). ^{13}C NMR spectrum (100 MHz) (220 K) (THF-d_8) δ=30.2 (t of m, ^1J=124.2 Hz, C5), 31.9 (t of m, ^1J=124.2 Hz, C6), 59.3 (dd, ^1J=167.2 Hz, ^2J=4.3 Hz, C2), 94.0 (ddd, ^1J=153.2 Hz, ^2J=3.9 and 3.9 Hz, C4), 139.2 (ddd, ^1J=140.4 Hz, ^2J=3.6 and 3.6 Hz, C3).

Financial support was provided by the Australian Government, APRA scholarship to L. G. and by the Japanese Government, JSPS postdoctoral fellowship to L. G. Dr. Nick Bampos is thanked for help with NMR acquisition and the NMR facility at the School of Chemistry, University of Sydney, is acknowledged for generous allocation of NMR time.

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