The Synthetic Utility of Sulfur-Containing Dianions

Kazuhiko Tanaka[a]; Aritsune Kaji[a]

[a] Department of Chemistry, Faculty of Science, Kyoto University, Kyoto, Japan

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THE SYNTHETIC UTILITY OF SULFUR-CONTAINING DIANIONS

Kazuhiko Tanaka and Aritsune Kaji

Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan

The reaction of organosulfur compounds with two or more equivalents of strong bases affords sulfur-containing dianions which react with a variety of electrophilic trapping agents. This review describes the utility of such reagents in organic synthesis.

I. INTRODUCTION

The potential usefulness of sulfur-containing carbanions has been widely recognized.[1-10] The widely used organosulfur carbanions are monometalated species derived from various types of sulfides, sulfoxides, and sulfones. Recently a variety of sulfur-containing dianions have been prepared and utilized as the efficient reagents for the synthesis of complex organic molecules. This review describes the utility of sulfur-containing dianions in synthetic organic chemistry.

II. THIOLS, DITHIOIC ACIDS, AND DITHIOATES

Thiols bearing an acidic hydrogen on the carbon atom can be converted to their C,S-dianions. Seebach and co-workers have reported that 2-propene-1-thiol (1) can be metalated to give a new reagent 2.[11,12]
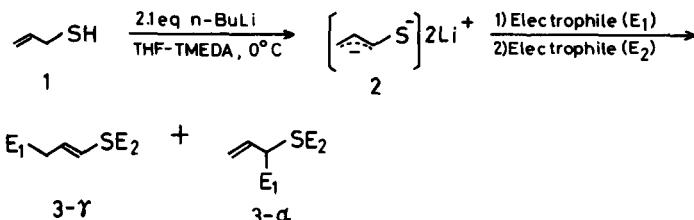
Thus, treatment of 1 with n-butyllithium gives the yellow-red dianion 2 which reacts with a variety of electrophilic reagents to afford mixtures of α- and γ-substituted products. Some representative examples are listed in Table I.

Reactions of Dianion 2 with Electrophiles

Electrophile		3	Product ratio
E_1	E_2	Yield(%)	3γ : 3α
$n\text{-}C_{10}H_{21}Br$	$n\text{-}C_{10}H_{21}Br$	90	77 : 23
$CH_2\!-\!C(CH_3)_2$ (epoxide)	$CH_2\!-\!C(CH_3)_2$ (epoxide)	86	78 : 22
C_2H_5CHO	CH_3I	69	74 : 26
$C_6H_5COCH_3$	CH_3I	95	70 : 30
CH_3SSCH_3	CH_3I	70	80 : 20

Vinyl sulfides (γ-isomers) are especially useful for a variety of syntheses as illustrated in Scheme 1.[12] Oxidative hydrolysis of 4 gives an aldehyde.[13]

$$n\text{-}C_6H_{13}\text{-}CH\!=\!CHSCH_3$$

$$\xrightarrow[\text{HCl}]{CH_3SH} n\text{-}C_6H_{13}CH_2CH(SCH_3)_2 \longrightarrow n\text{-}C_6H_{13}CH_2CHO$$

$$\xrightarrow[\text{CH}_3\text{OH}]{HgCl_2} n\text{-}C_6H_{13}CH_2CH(OCH_3)_2$$

$$\xrightarrow[\text{CH}_3\text{OH}]{NBS} n\text{-}C_6H_{13}CHBrCH(OCH_3)_2$$

$$\xrightarrow[\text{CH}_3\text{CN-H}_2\text{O}]{NBS} n\text{-}C_6H_{13}CHBrCHO$$
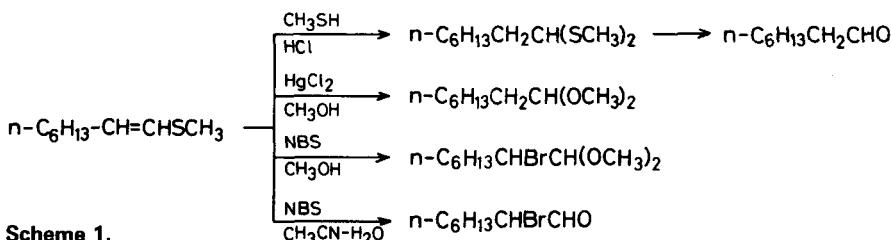
Scheme 1.

An efficient procedure for the regioselective reaction of the dianion of 2-propene-1-thiol with carbonyl compounds has recently been developed by Seebach and co-workers.[14,15] The magnesium derivative 5 prepared from dianion 2 and 1 equivalent of magnesium bromide react at the α-position to sulfur to afford a hydroxy sulfide 6 (Table II).[14,15]

$$2 \xrightarrow{MgBr_2} \left[\text{\textasciitilde}\!\!\sim\!\!S^-\right]Mg^{2+} \xrightarrow[\text{2) CH}_3\text{I}]{\text{1) R}_1\text{R}_2\text{C=O}} R_1\!-\!\underset{R_2}{\overset{OH}{C}}\!\!\text{\textasciitilde}\!\!SCH_3$$

5   6
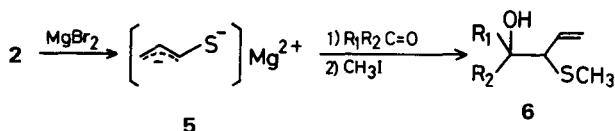
TABLE II

Regioselective Reactions of Dianion 5
with Carbonyl Compounds

Carbonyl compds		6	7
R_1	R_2	(%)	(%)
C_2H_5	H	91	48
$CH_3CH\!=\!CH$	H	95	47
$-(CH_2)_4-$		94	78
C_6H_5	CH_3	89	70
$-CH\!=\!CH(CH_2)_3-$		91	75

β-Hydroxy sulfides **6** can be converted to epoxides **7**,[15,16] ketones,[15] or olefins.[17]
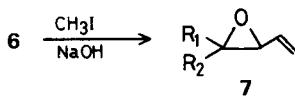
Dianion **8** also reacts with carbonyl compounds at the α-carbon atom.[15]
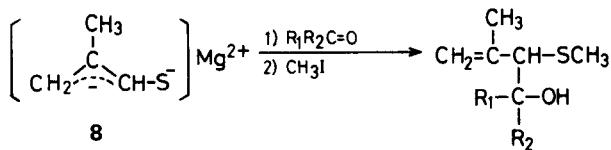
The dianion **9** of phenylmethanethiol can be generated by treatment of 2.1 equivalents of n-butyllithium in THF with N,N,N',N'-tetramethylethylenediamine (TMEDA) as a consolvent and reacts with electrophiles both at carbon and sulfur (Table III).[12,18]
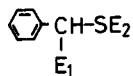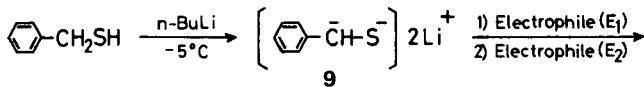

TABLE III

Reactions of Dianion 9 with Electrophiles

| Electrophile		Product (10)	Yield (%)
E_1	E_2		
$(CH_3)_3SiCl$	$(CH_3)_3SiCl$	$C_6H_5CH\langle{}^{SSi(CH_3)_3}_{Si(CH_3)_3}$	93
C_6H_5CHO	CH_3I	$C_6H_5CH\langle{}^{SCH_3}_{CH(OH)C_6H_5}$	82
CH_3I	CH_3I	$C_6H_5CH\langle{}^{SCH_3}_{CH_3}$	72
$(CH_3)_2C\!-\!CH_2$ over O	$(CH_3)_2C\!-\!CH_2$ over O	$C_6H_5CHSCH_2C(OH)(CH_3)_2$ / $CH_2C(OH)(CH_3)_2$	70
$\langle{}\rangle{=}O$	CH_3I	$C_6H_5CH\!-\!SCH_3$ / $\langle\rangle\!-\!OH$	76

The generation of another type of phenylmethanethiol dianion can be carried out at $-100°C$. Addition of **11** to cyclohexanone followed by acid-catalyzed cyclization gives a spiroisobenzotetrahydrothiophene derivative **12**.[19]

11

60%   12 (56%)
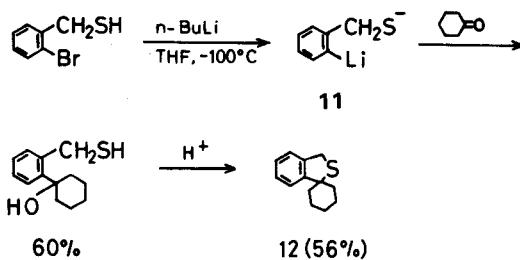
The dianion **14** of 8-chloro-1-naphthalenethiol is highly reactive toward elemental sulfur, selenium, and tellurium.[20] The products (**15a, 15b**, and **15c**) are good electron donors and form charge-transfer complexes both with 7,7,8,8-tetracyanoquinodimethane and iodine.

13   14

15a M = S   44%
15b M = Se 65%
15c M = Te 60%
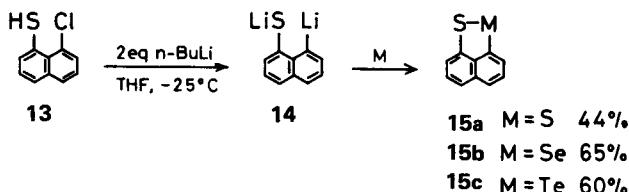
However, the monoanion of 8-chloro-1-(methylthio)-naphthalene (**16**) does not react with such electrophiles under reaction conditions identical with those for the dianion **14**.

16
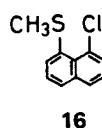
Reaction of ketones with carbon disulfide in the presence of 2 equivalents of lithium 4-methyl-2,6-di-*t*-butylphenoxide, followed by the addition of methyl iodide produces the dithiomethylene derivative **17**.[21]
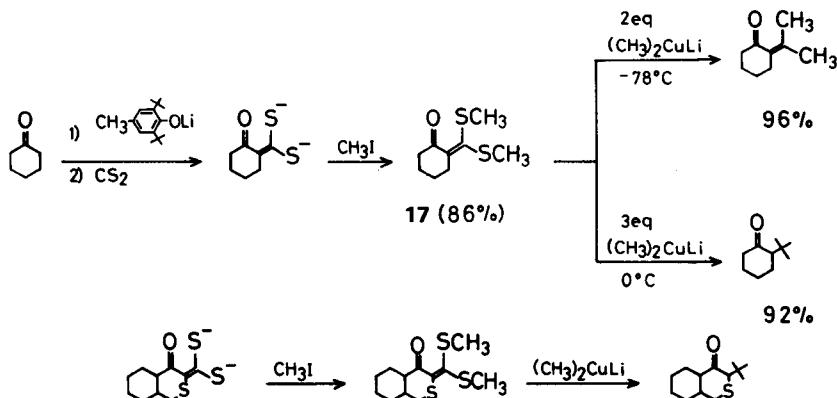
The dithiomethylene groups can be transformed into isopopylidene or *t*-butyl moieties by conjugate addition of lithium dimethylcuprate.[21,22] Such a procedure was employed in the sythesis of dithiomethylene derivatives of carboxylic esters **18**.[23]
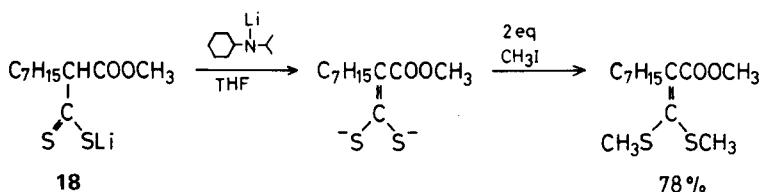
The reaction of dianion **19** with allyl bromide produces **20** in 49% yield.[24]
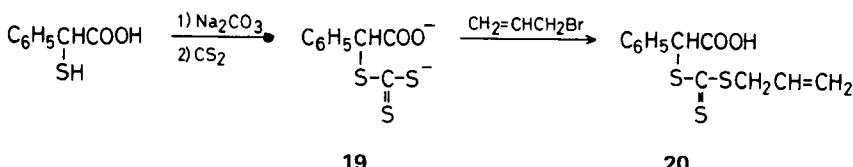
The dithioic acid can be metalated with 2 equivalents of lithium diisopropylamide.[25] Alkylation of the S,S-dianion **21** gives dithioacetals **22** which can be converted to aldehydes or a variety of carboxylic acid derivatives as illustrated in Scheme 2.[3,7]

Scheme 2.
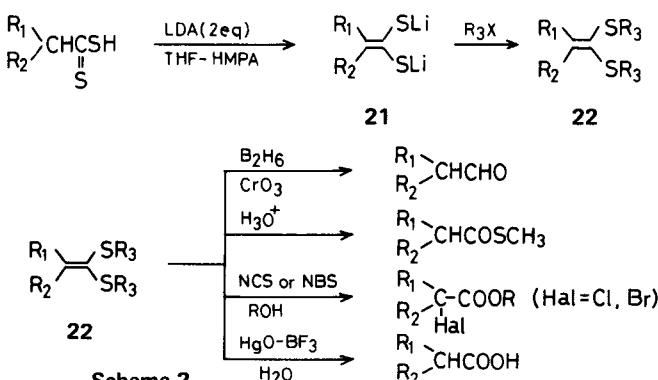
Table IV shows the synthesis of a variety of dithioacetals.

TABLE IV

Alkylations of Diantion 21

R_1	R_2	R_3	Product(22)	Yield(%)
H	H	C_2H_5I		97
H	H	$BrCH_2CH_2CH_2Cl$		45
H	CH_3	$BrCH_2CH_2CH_2Cl$		54
$-(CH_2)_5-$	C_2H_5I			87
$-(CH_2)_5-$	$BrCH_2CH_2CH_2Cl$			51

The reaction of dithioesters **23** with potassium hydride–s-butyllithium gives the C,S-dianions **24** which can react with a variety of carbonyl compounds at the ω-carbon (Table V).[26]

23a R= CH₃

23b R= CH(CH₃)₂

24a R= CH₃

24b R= CH(CH₃)₂

25
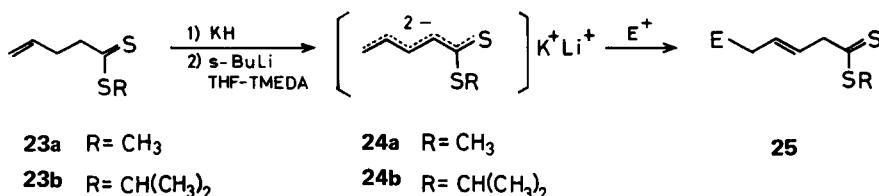
TABLE V

Reactions of Dianion 24 with Carbonyl Compounds

Dianion 24	Carbonyl compd.	Product(25) yield (%)
24a	C₆H₅CHO	43
24a	(C₆H₅)₂CO	71
24b	CH₃CH₂CHO	56
24b	(C₆H₅)₂CO	84
24b	⬠=O	44

Since dithioacetals can be converted to carbonyl compounds,[3,7] this method constitutes an efficient route to dienone derivatives as illustrated by the conversion **24b→26**.

24b

80%

26 (57%)
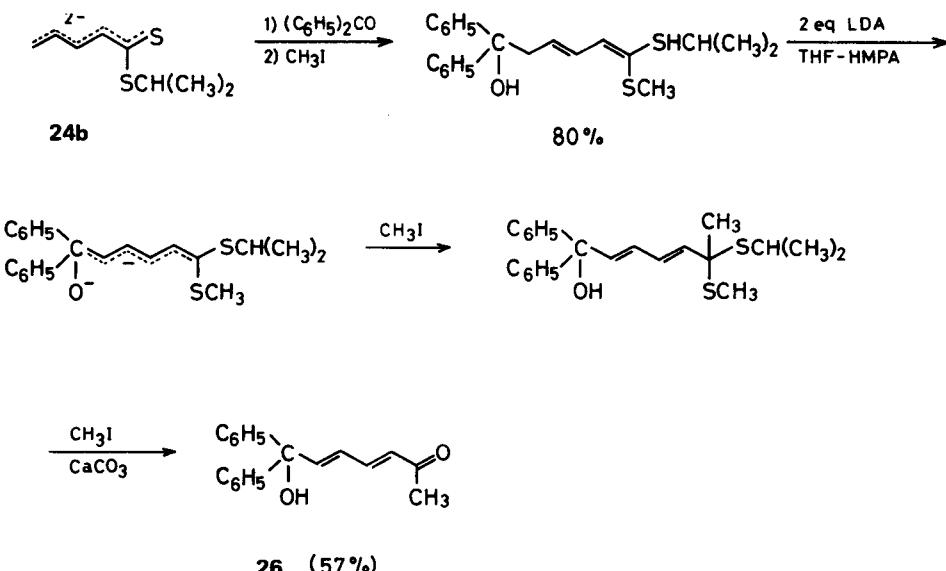
Cleavage of 2*H*-thiopyran by sodium naphthalenide produces the dianion which can be trapped with methyl iodide to afford a mixture of 1-methylthio-1,3-hexadiene and 1-methylthio-3-methyl-1,4-pentadiene in 75% yield.[27]

$$\underset{S}{\bigcirc} \xrightarrow[\text{THF}]{\text{NaC}_{10}\text{H}_7} \overset{-}{S}-\text{CH}-\text{CH}-\text{CH}-\overset{-}{\text{CH}}-\text{CH}_2 \xrightarrow[\text{THF}]{\text{CH}_3\text{I}} \underset{H}{\overset{\text{CH}_3\text{S}}{\diagup}}\diagdown\underset{H}{\overset{\text{CH}=\text{CH}-\text{CH}_2\text{CH}_3}{\diagup}}$$

$$+\ \underset{H}{\overset{\text{CH}_3\text{S}}{\diagup}}\diagdown\underset{H}{\overset{\text{CH}(\text{CH}_3)\text{CH}=\text{CH}_2}{\diagup}}$$
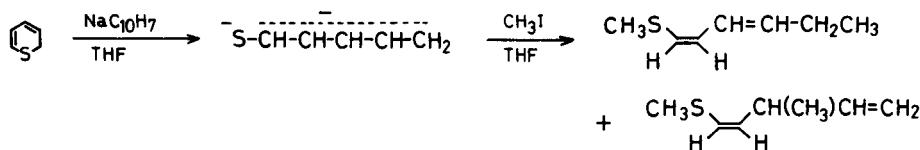
The generation of dianion **27** can be accomplished by treatment of commercially available ethyl 2-mercaptoacetate with lithium diisopropylamide at $-78°$C. The dianion **27** is reactive toward alkylation and adds to the carbonyl groups of aldehydes and ketones.[28]

$$\text{HSCH}_2\text{COOEt} \xrightarrow[\text{THF-TMEDA}]{2.2\,\text{eq LDA}} \left[\ \overset{-}{\text{S}}-\overset{-}{\text{C}}\text{HCOOEt}\ \right]\,2\,\text{Li}^+$$

27

$$\xrightarrow{\text{CH}_3\text{I}} \underset{\text{CH}_3}{\overset{|}{\text{CH}_3\text{SCHCOOEt}}} \qquad 86\%$$

$$\xrightarrow{\text{CH}_2=\text{CHCH}_2\text{Br}} \underset{\text{CH}_2\text{CH}=\text{CH}_2}{\overset{|}{\text{CH}_2=\text{CHCH}_2-\text{SCHCOOEt}}} \qquad 64\%$$

$$\xrightarrow{(\text{CH}_3)_2\text{CO}} \underset{\text{CH}_3}{\overset{\text{HO\ \ \ SH}}{\underset{|}{\overset{|\ \ \ \ \ |}{\text{CH}_3\text{-C}-\text{CHCOOEt}}}}} \qquad 82\%$$
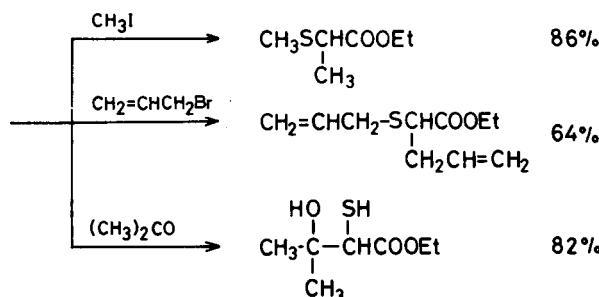
Taking advantage of a facile thiirane formation and subsequent elimination of elemental sulfur, a new route to α,β-unsaturated carboxylic esters **29** has been developed.[29]

$$\underset{R_1}{\overset{|}{\overset{-}{\text{S}}-\overset{-}{\text{C}}-\text{COOEt}}} \xrightarrow[\text{2) CICOOEt}]{\text{1) R}_2\text{R}_3\text{CO}} \underset{R_3}{\overset{R_2}{\diagup}}\diagdown\underset{\text{COOEt}}{\overset{R_1}{\diagup}}$$

28   **29**
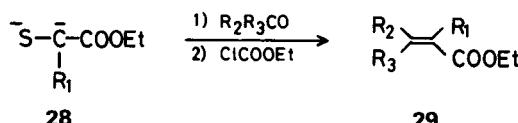
Representative results are collected in Table VI.

TABLE VI

Synthesis of α,β-Unsaturated Esters **29** from Dianion **28** and Carbonyl Compounds

| Dianion 28 R_1	Carbonyl compound	Product 29	Yield (%)	E / Z
H	2-Butanone	$\underset{\text{CH}_3\text{CH}_2}{\overset{\text{CH}_3}{\diagup}}\diagdown\underset{\text{COOEt}}{\overset{\text{H}}{\diagup}}$	64	43/57
H	Acetophenone	$\underset{\text{C}_6\text{H}_5}{\overset{\text{CH}_3}{\diagup}}\diagdown\underset{\text{COOEt}}{\overset{\text{H}}{\diagup}}$	58	97/3
H	2-Hexanone	$\underset{n\text{-C}_4\text{H}_9}{\overset{\text{CH}_3}{\diagup}}\diagdown\underset{\text{COOEt}}{\overset{\text{H}}{\diagup}}$	67	38/62
CH$_3$	Benzaldehyde	$\underset{\text{Ph}}{\overset{\text{H}}{\diagup}}\diagdown\underset{\text{COOEt}}{\overset{\text{CH}_3}{\diagup}}$	45	53/47
CH$_3$	2-Butanone	$\underset{\text{CH}_3\text{CH}_2}{\overset{\text{CH}_3}{\diagup}}\diagdown\underset{\text{COOEt}}{\overset{\text{CH}_3}{\diagup}}$	59	23/77

In contrast to the facile reaction of ethyl 2-mercaptoacetate, when ethyl glycolate was treated in a similar manner as described above, the adduct was obtained only in 15% yield.

$$HOCH_2COOEt \xrightarrow[\text{2) } (CH_3)_2CO]{\text{1) LDA}} \begin{array}{c} HO \ \ OH \\ | \ \ \ | \\ CH_3-C-CHCOOEt \\ | \\ CH_3 \end{array}$$
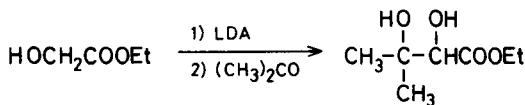
Reaction of ethyl 3-mercaptoacetate with lithium bis-(trimethylsilyl)-amide at $-78°C$ in THF produces the C,S-dianion **30** which can be trapped with cyclohexanone and methyl iodide.[30]

$$HSCH_2CH_2COOEt \xrightarrow{\text{2.2eq } LiN(SiMe_3)_2} \left[^-S-CH_2\bar{C}HCOOEt \right] 2Li^+ \xrightarrow[\text{2) } CH_3I]{\text{1)}}$$

30

OH
CH-COOEt   68%
CH₂SCH₃
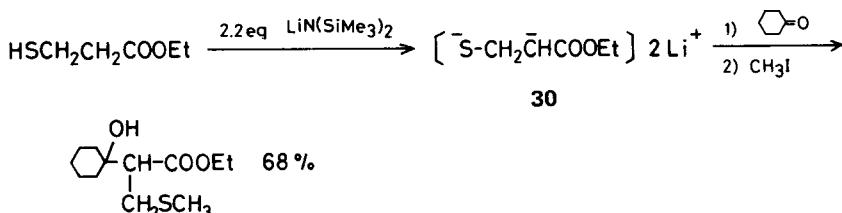
The dianion **32** of α-mercapto-γ-butyrolactone is also reactive toward alkyl halides and carbonyl compounds.[31,32]

$$\underset{31}{\text{SH}} \xrightarrow[\text{THF-TMEDA}]{\text{2.2eq LDA}} \underset{32}{\left[\text{S}^- \right]} 2Li^+ \xrightarrow{RX} \underset{33}{\text{R SR}}$$

| **33** | RX = CH₃I | 93% |
| | RX = CH₃CH₂I | 73% |
| | RX = CH₂=CHCH₂Br | 90% |
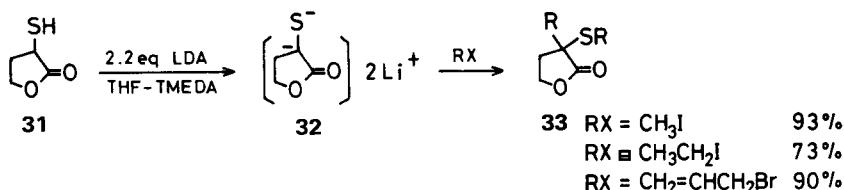
Evidence for the dianion **32** comes from the isolation of the dialkylated products **33**. The one-pot stereoselective synthesis of α-alkylidene-γ-butyrolactones using dianion **32** has been reported (Table VII).

TABLE VII

Stereoselective Syntheses of α-Alkylidene-γ-butyrolactones

Carbonyl compound	Product 36	Yield (%)	E : Z
Benzaldehyde	C₆H₅ / H	54	100 : 0
Pentanal		69	95 : 5
Hexanal		64	97 : 3
Acetophenone	C₆H₅ / CH₃	40	100 : 0
Acetone	CH₃ / CH₃	50	—

The mechanism proposed for the formation of **36** from the dianion **32** is considered to involve initially adduct **34** which can react with ethyl chloroformate to give α-alkylidene-γ-butyrolactones via the thiirane intermediate **35**.
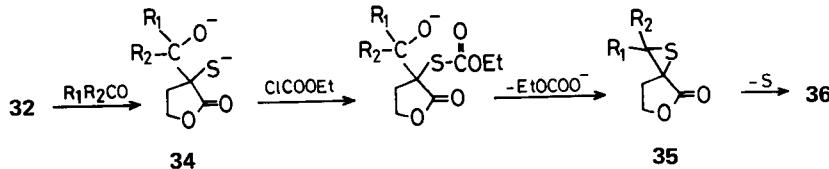
Formation of **34** from pentanal when followed by reaction with methyl iodide gives α-(1-hydroxypentyl)-α-methylthio-γ-butyrolactone in 84% yield.
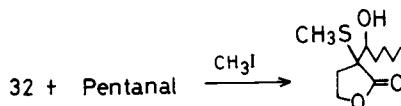
Intermediates such as **34** can be trapped when the reaction mixture of the dianion **32** and a carbonyl compound is quenched with saturated aqueous ammonium chloride solution at −78°C as shown in Scheme 3.

R = C₆H₅   76 %
R = CH₃(CH₂)₂ 87 %

34a R = C₆H₅
34b R = CH₃(CH₂)₂

36a R = C₆H₅   35 % (E/Z = 100/0)
36b R = CH₃(CH₂)₂ 42 % (E/Z = 96/4)
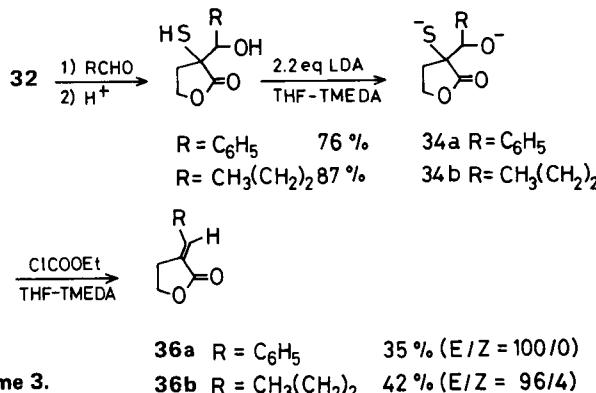
Scheme 3.

The reaction of **34** with 2.2 equivalents of lithium diisopropylamide/TMEDA at −78°C in THF, followed by addition of ethyl chloroformate gives predominantly the E-isomer **36**.

III. SULFIDES

The reaction of 2-(2-propynylthio)-thiazoline with n-butyllithium gives a new dianion **37** which can be trapped with active alkylating agents such as benzyl, allyl, or 2-propynyl bromide to afford **38**.

37   38
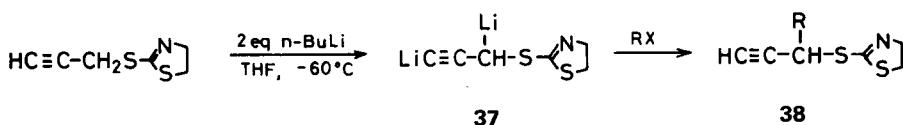
Desulfurization of the adduct with zinc in acetic acid gives a mixture of **39** and **40** in a ratio of 1:8.[33]

$$C_6H_5C{\equiv}C\text{-}CH_2CHS \underset{HC{\equiv}C}{-}\left\{^N_S\right] \xrightarrow{\text{Zn}} C_6H_5C{\equiv}CCH_2CH_2C{\equiv}CH \; + \; C_6H_5C{\equiv}CCH_2CH{=}C{=}CH_2$$

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \textbf{39} \qquad\qquad\qquad\qquad\qquad \textbf{40}$$
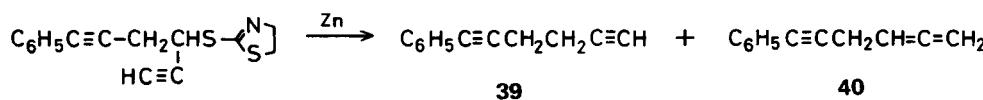
Nozaki and co-workers have reported an efficient procedure for the stereoselective synthesis of trisubstituted olefins.[34] Alkylation of the dianion **41** takes place regioselectively at the α-position to afford **42** which undergoes a facile rearrangement to the E-dithioate **43**.

$$\textbf{41} \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \textbf{42}$$

$$\textbf{43} \qquad\qquad\qquad\qquad\qquad\qquad \textbf{44} \quad (63\%)$$
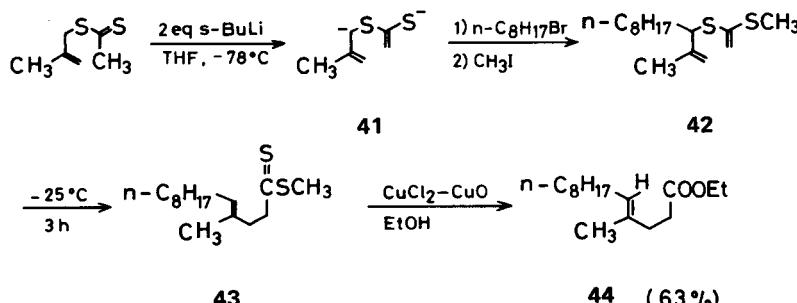
Conversion of the dithioester **43** to ethyl (E)-4-methyl-4-tridecenoate (**44**) can be achieved in good yield with cupric chloride and cupric oxide in ethanol. The reaction of dianion **45** with n-octyl bromide under similar conditions gives the (E)-ester **46** in 70% overall yield.

$$\textbf{45} \qquad\qquad\qquad\qquad\qquad\qquad\qquad \textbf{46}$$
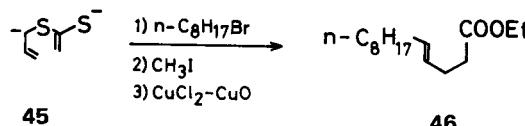
The dianion **47** of (methylthio)-acetic acid has recently been employed as a highly useful acyl anion equivalent.[35-38]

$$CH_3SCH_2COOH \xrightarrow[\text{THF-HMPA}]{\text{2.4eq LDA}} \left[CH_3S\bar{C}HCO_2^- \right] 2Li^+ \xrightarrow{RX} CH_3S{-}\overset{R}{\underset{|}{C}}HCOOH$$

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad \textbf{47} \qquad\qquad\qquad\qquad\qquad\qquad \textbf{48}$$
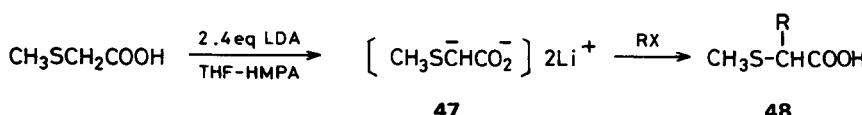
The reaction of **47** with alkylating agents gives α-alkylated carboxylic acids **48** as shown in Table VIII.

TABLE VIII

Alkylations of Dianion 47

Alkyl halide	Product 48	Yield(%)
(CH₃)₂CH-CH₂Br	SCH_3 $(CH_3)_2CHCH_2\overset{|}{C}HCOOH$	80
(CH₃)₂CH-I	SCH_3 $(CH_3)_2CH\overset{|}{C}HCOOH$	59
$Cl(CH_2)_{10}CH_2I$	SCH_3 $Cl(CH_2)_{10}CH_2\overset{|}{C}HCOOH$	69

Treatment of the dianion **49** derived from **48** with alkyl halides followed by oxidative decarboxylation[38] gives the ketones **51** in good yields.
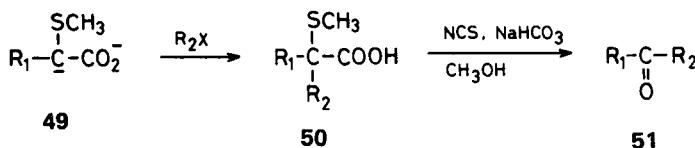
The results are listed in Table IX.

TABLE IX
Alkylations of Dianion 49 with Subsequent Oxidative Decarboxylation

Dianion 49 R_1	R_2X	50 Yield(%)	Ketone 51	Yield (%)
$(CH_3)_2CHCH_2-$		71		66
$(CH_3)_2CHCH_2-$		46		95
$(CH_3)_2CH-$	$C_6H_5CH_2Br$	63		80

Another attractive procedure for the synthesis of the vinyl sulfides **54** from the dianion **52** involves the alkylation and subsequent oxidative decarboxylation of **53** (Table X).[39]
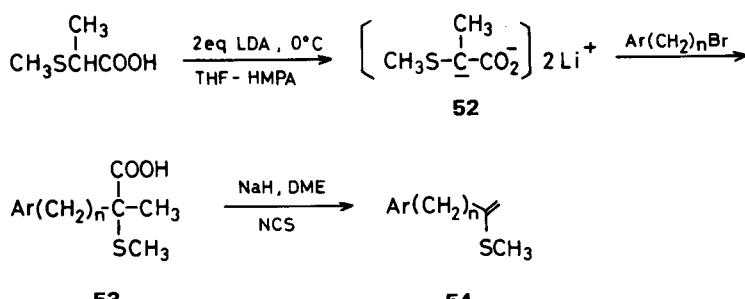
TABLE X
Syntheses of Vinyl Sulfides 54

Ar	n	53 Yield(%)	54 Yield(%)
Ph	2	57	82
Ph	3	60	85
	3	66–85	84–100
	4	74–95	85
	5	74	85

As mentioned before (Section II), vinyl sulfides can be hydrolyzed to carbonyl compounds.[40–42]

The dilithio derivative **55** of (phenylthio)-acetic acid has been shown to be highly reactive toward epoxides to give γ-butyrolactones **56**, while the reaction of monoanion **59** with 1,2-epoxypropane gives the corresponding γ-butyrolactone in 36% yield.[43,44]
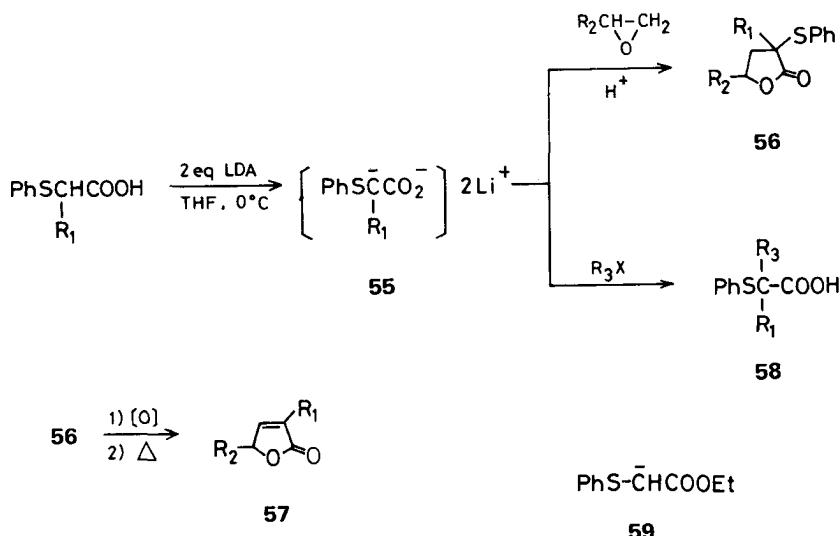
α-Sulfenylated γ-butyrolactones can be converted to the $\Delta^{\alpha,\beta}$-butenolides **57** by oxidation and subsequent dehydrosulfenylation[37,38] (Table XI).

TABLE XI

Syntheses of Lactones from Dianion 55

Dianion 55	Epoxide	Product 56	Yield (%)	Product 57	Yield (%)
$PhS\bar{C}HCO_2^-$	$CH_3(CH_2)_3CH{-}CH_2$ (O)		94		82
$PhS\bar{C}HCO_2^-$			68		82
$PhS\bar{C}HCO_2^-$	$PhCH{-}CH_2$ (O)		94		80
$PhS\bar{C}CO_2^-$ | CH_3	$CH_3(CH_2)_3 CH{-}CH_2$ (O)		88		63
$PhS\bar{C}CO_2^-$ | C_2H_5	$CH_3(CH_2)_3CH{-}CH_2$ (O)		73		78

Of course, the dianions **55** also react with a variety of alkyl halides to afford α-sulfeny-lated carboxylic acids which allow a number of useful synthetic transformations.[43,45]
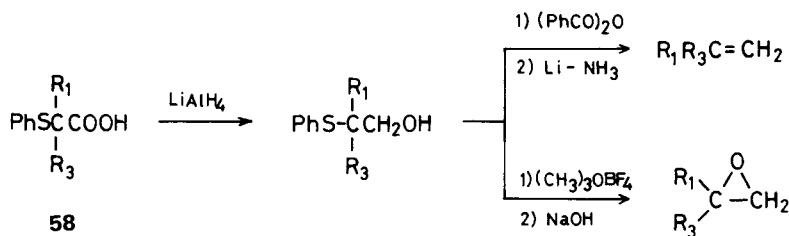
Representative results of the alkylation of dianion **55** are collected in Table XII.

TABLE XII

Alkylations of Dianion 55

Dianion 55	Alkyl halide	Product 58	Yield (%)
PhSĊHCO$_2^-$	CH$_3$(CH$_2$)$_{11}$I	CH$_3$(CH$_2$)$_{11}$CHCOOH, SPh	98
	Br(CH$_2$)$_4$Br	(cyclopentane) SPh, COOH	75
	C$_2$H$_5$Br	CH$_3$CH$_2$CHCOOH, SPh	~100
CH$_3$(CH$_2$)$_{11}$ĊCO$_2^-$, SPh	CH$_3$I	CH$_3$(CH$_2$)$_{11}$CHCOOH, CH$_3$, SPh	98
CH$_3$(CH$_2$)$_3$ĊCO$_2^-$, SPh	C$_{10}$H$_{17}$Br	CH$_3$(CH$_2$)$_3$CHCOOH, C$_{10}$H$_{17}$, SPh	90

C$_{10}$H$_{17}$Br = geranyl bromide

The dimetalations and subsequent electrophilic trapping of sulfides are listed in Table XIII.

The dianion **60** undergoes intramolecular alkylation to give the tetrahydrothiophene derivative **61**.[53]
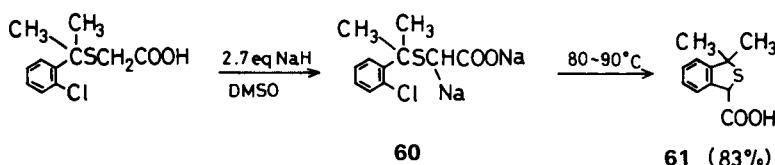
Whitlock and coworkers have found elegant cycloacylations of dianions as illustrated by the conversions **62→63** and **64→65**.[54]

TABLE XIII
### Formation of Sulfide-Containing Dianions with Electrophiles

Reactant	Base	Solvent	Dianion	Electrophile	Product	Yield (%)	Ref.
1,3-dithiane-2-COOH	LDA	THF	dithiane-C(Li)(CO$_2$Li)	cyclohexenyl-Br	dithiane-2-(cyclohexenyl)-CO$_2$H	85	46
				CH$_2$=CHCH$_2$Br	dithiane-2-(allyl)-CO$_2$H	90	46
dithiane-CH$_2$OH	n-BuLi	THF	dithiane-C(Li)-CH$_2$OLi	sugar-CHO	dithiane-CH$_2$OH-CH(OH)-sugar	54	47
CH≡CCH$_2$SCHC$_2$H$_5$	n-BuLi	THF	LiC≡CCHSCHC$_2$H$_5$ Li	CH$_3$I	CH$_3$C≡C—CH$_3$S—C$_2$H$_5$	82	48
C$_6$H$_5$-C=N- thiophene	n-BuLi	Ether	C$_6$H$_5$-C=NLi thiophene-S-Li	C$_6$H$_5$CN	thiophene-S-COC$_6$H$_5$ (C$_6$H$_5$COC$_6$H$_5$)	47	49,50

TABLE XIII continued

Reactant	Base	Solvent	Dianion	Electrophile	Product	Yield (%)	Ref.
CH_3 $\left[\begin{smallmatrix}S & S\\S & S\end{smallmatrix}\right]$	LDA	Ether	$CH_3\left[\begin{smallmatrix}S & S\\S & S\end{smallmatrix}\right]^{Li}_{Li}$	$ClCO_2Et$	$CH_3\left[\begin{smallmatrix}S & S\\S & S\end{smallmatrix}\right]{<}^{CO_2Et}_{CO_2Et}$	30	51
$C_6H_5SCH_2\overset{\underset{\parallel}{O}}{C}NH$–C$_6H_{11}$	NaH	DMF	$C_6H_5S\overset{Na}{C}H\overset{Na}{C}N$–C$_6H_{11}$ $\overset{O}{\parallel}$	CH_2I_2	C$_6$H$_5$S–[β-lactam]–N–C$_6$H$_{11}$, $=O$	54	52
$C_6H_5SCH_2\overset{\underset{\parallel}{O}}{C}NH$–n-Bu	NaH	DMF	$C_6H_5S\overset{Na}{C}H\overset{Na}{C}N$–n-Bu $\overset{O}{\parallel}$	CH_2I_2	C$_6$H$_5$S–[β-lactam]–N–n-Bu, $=O$	38	52
$C_6H_5SCH_2\overset{\underset{\parallel}{O}}{C}NH$–CH$_2C_6H_5$	NaH	DMF	$C_6H_5S\overset{Na}{C}H\overset{Na}{C}N$–CH$_2C_6H_5$ $\overset{O}{\parallel}$	CH_2I_2	C$_6$H$_5$S–[β-lactam]–N–CH$_2$C$_6$H$_5$, $=O$	27	52
$C_6H_5SCH_2\overset{\underset{\parallel}{O}}{C}NH$–i-Bu	NaH	DMF	$C_6H_5S\overset{Na}{C}H\overset{Na}{C}N$–i-Bu $\overset{O}{\parallel}$	CH_2I_2	C$_6$H$_5$S–[β-lactam]–N–iBu, $=O$	28	52

62   **63 (67%)**

64   **64**

65 (55%)
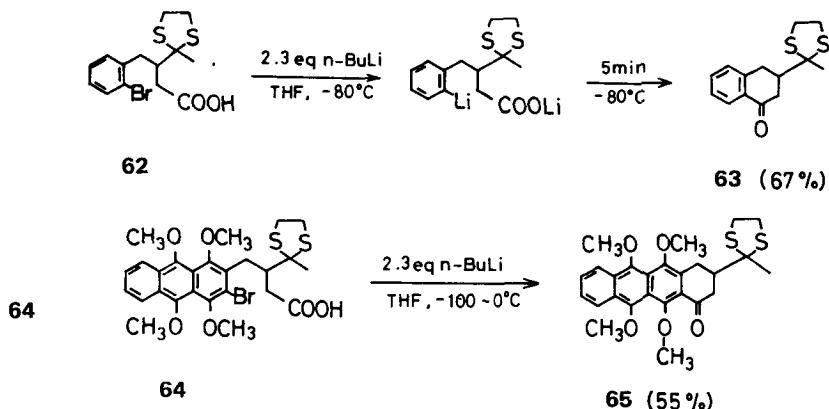
The formation of cycloalkanes and cycloalkenes is readily accomplished by the dianion route. For example, **66** gives cyclopentene **67** upon treatment with excess methyllithium in THF-TMEDA at 0°C, and **68** gives cyclobutene **69** under the same reaction conditions.[55]

66

67 (52%)

68

69 (47%)
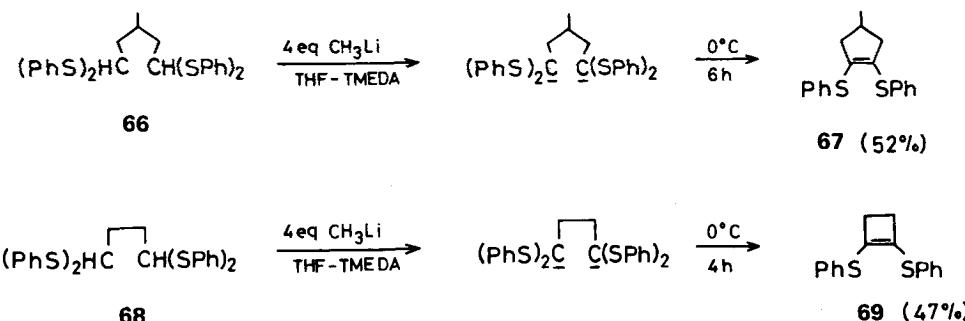
The dianion **71** has been postulated as an intermediate in the conversion of 2-hydroxy-1,3-bis-(phenylthio)-propane (**70**) to the corresponding cyclopropanol with n-butyllithium.[56]

70   **71**   **79%**
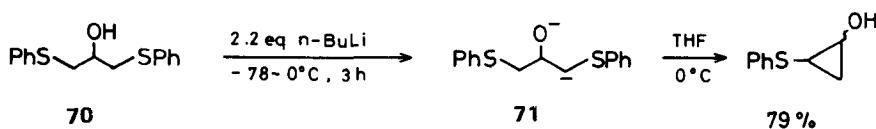
The allylic dianion **72** has potential utility in the stereoselective synthesis of disubstituted olefins. Treatment of ethyl (allylthio)-acetate with lithium diisopropylamide followed by addition of s-butyllithium at −78°C gives the novel dianion **72** which can be trapped with alkyl halides to afford a mixture of α- and γ-isomer as shown in Table XIV.


72

73-α

73-γ
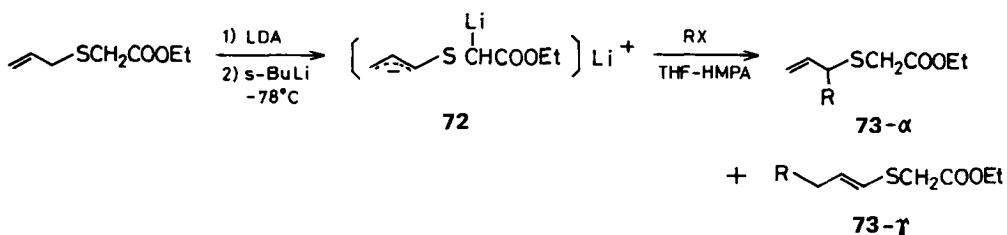
TABLE XIV

Alkylations of Dianion 72

Alkyl halide	73 Yield (%)	73α : 73γ
CH$_3$(CH$_2$)$_4$Br	69	80 : 20
(CH$_3$)$_2$CH(CH$_2$)$_2$Br	63	78 : 22
CH$_3$(CH$_2$)$_7$Br	59	71 : 29
CH$_3$(CH$_2$)$_6$Br	57	82 : 18
CH$_3$(CH$_2$)$_5$Br	66	80 : 20

The method for the conversion of the α-isomer to the (E,E)-dienoate **74** is illustrated below.[57]

74 (77%)
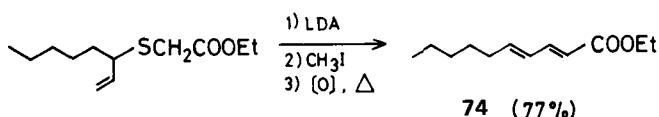
The (E,E)-dienoate **74** is a key intermediate for pellitorine.[58,59]

IV. SULFOXIDES AND SULFINAMIDES

The dianion **75** has been found to be a very convenient reagent for the methylenation of carbonyl compounds.[60] The reaction of **75** with a variety of carbonyl compounds in THF affords β-hydroxy sulfoxides in high yields.

75
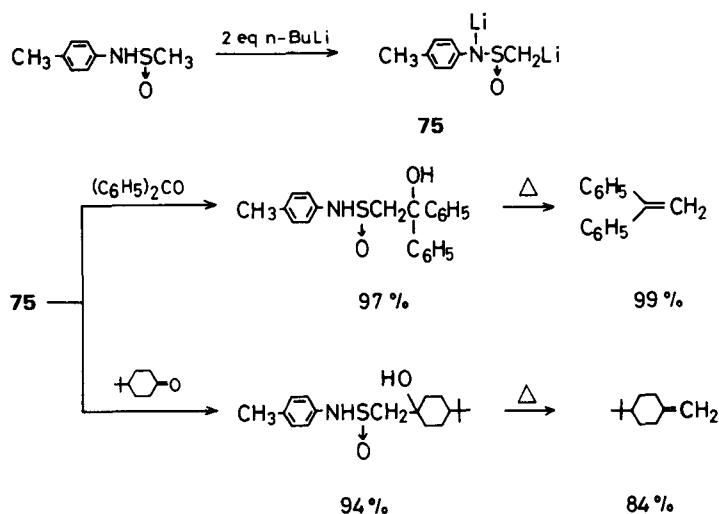
Thermal decomposition of β-hydroxy sulfoxides in dry toluene gives olefins in good to excellent yields. Similar ylidenation of carbonyl groups can be carried out using dianion **76**.

76   **55 %**   **77 (98%)**
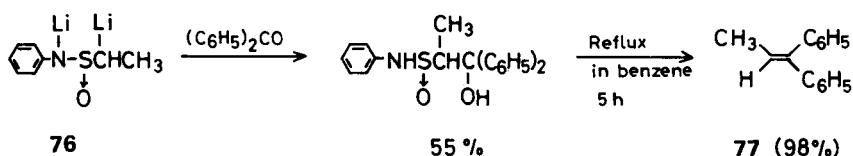
β-Keto sulfoxides, which can be prepared by condensation of sulfoxides and esters,[61] can be metalated with sodium hydride and n-butyllithium yielding a stabilized dianion such as **78**.[62,63] The sequence is illustrated by the preparation of dihydrojasmone **79**.[62]

78

79 (57 %)
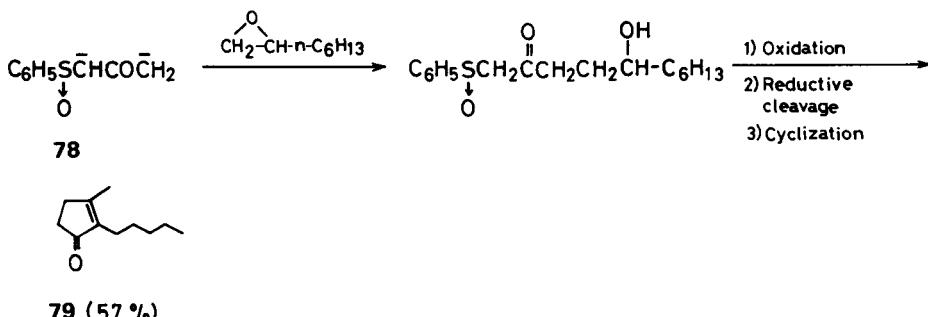
The reaction of dianion **80** with alkyl halides is useful in producing vinyl ketone derivatives **82** in good yields[64] (Table XV).

80   **81**


82
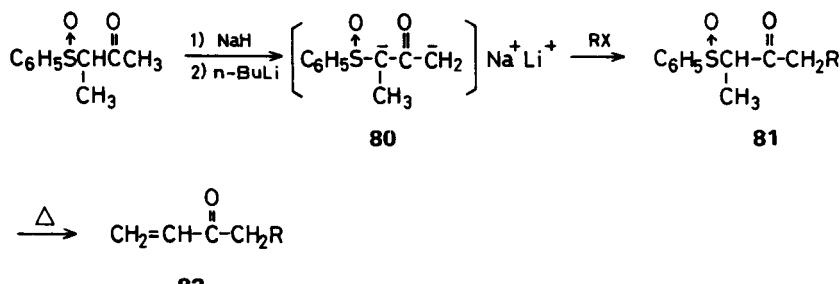
TABLE XV

Alkylations of Dianion 80 and Subsequent Dehydrosulfenylations

Alkyl halide	81 Yield(%)	82 Yield(%)
CH₃I	65	78
C₆H₅CH₂Br	72	75
Geranyl chloride	71	92
n-C₄H₉I	84	78
CH₃ClC=CHCH₂Cl	70	98

An example of the use of the dianion **83** in the synthesis of *dl*-muscone is shown.[65,66]

83   **70%**   **90%**
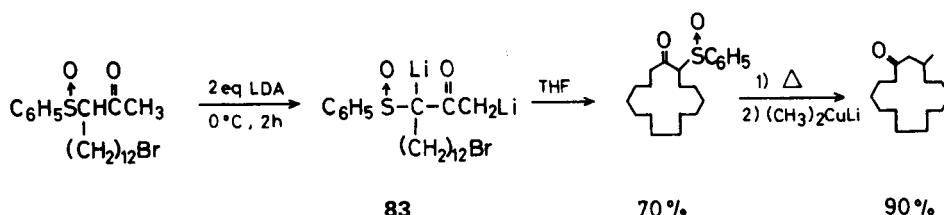
Alkylation of the dianion **84** with alkyl halides provides a route to the substituted cyclopentenone derivatives **85**.[66]

84   **85**

R = n-Bu   65%   43%

R = C$_6$H$_5$CH$_2$ 50%   55%
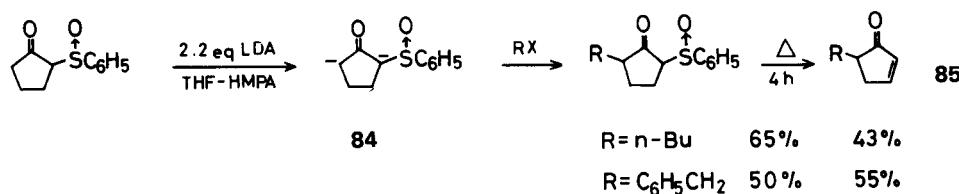
Evans and coworkers have reported an efficient synthetic method for 1-alkyl-1-cyclopentene-cis-3,5-diols, useful intermediates in prostaglandin synthesis, utilizing the new dianion **87** (Table XVI).[67]

86   **87**   **88**

89   **90**
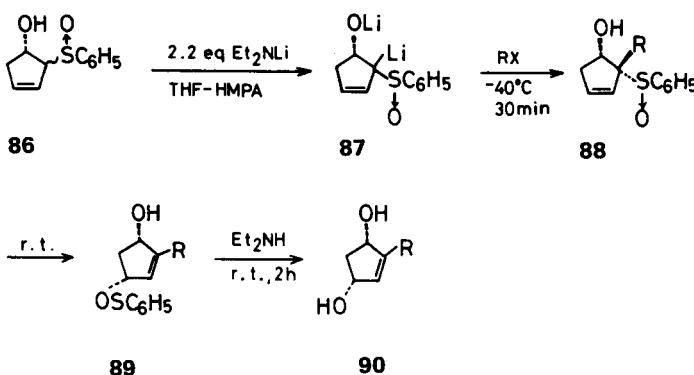
TABLE XVI

Syntheses of 1-Alkyl-1-cyclopentene-cis-3,5-diols
90

Alkyl halide	90 Yield(%)
CH$_3$(CH$_2$)$_5$I	50~60
[O,O]-(CH$_2$)$_6$I	54
I(CH$_2$)$_6$COO-t-Bu	45
BrCH$_2$C≡C(CH$_2$)$_3$COO-t-Bu	33
C$_6$H$_5$CH$_2$Br	50

The alkylated sulfoxides **88** undergo facile rearrangement to the sulfenate esters **89**[68] which give **90** after hydrolysis with diethylamine.[69]

The dianion of a hydroxy sulfoxide is useful as a terpene building block. Treatment of a **91** with 2 equivalents of n-butyllithium affords the dianion which reacts with 1-bromo-3-methyl-butene to afford **93** in 90% yield.[70]
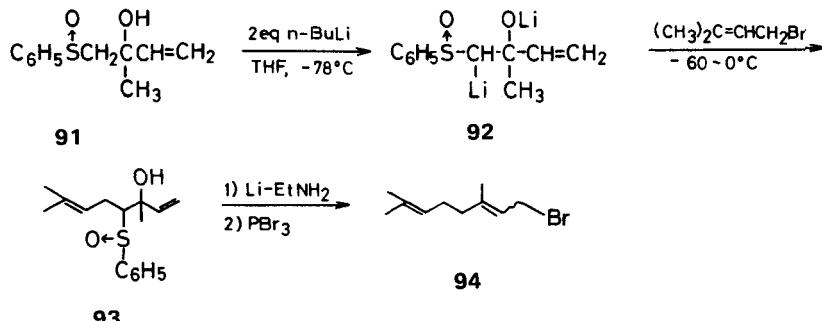
The hydroxy sulfoxide **93** can be converted to a mixture of geranyl and neryl bromide (**94**) in 70% yield.

V. SULFONES AND SULFONYLHYDRAZONES

Since the α-hydrogen of sulfone derivatives is the most acidic, a great number of sulfone-containing dianions are known. The generation and reactions of such dianions are covered in the excellent review by Kaiser *et al.*[2]

In this review, the most recent advances with sulfone-containing dianions will be described.

The dianion **96** of a hydroxy sulfone can be readily generated on treatment with 2 equivalents of n-butyllithium and serve as a useful tool for the synthesis of Vitamin A (**98**) as illustrated in Scheme 4.[71]
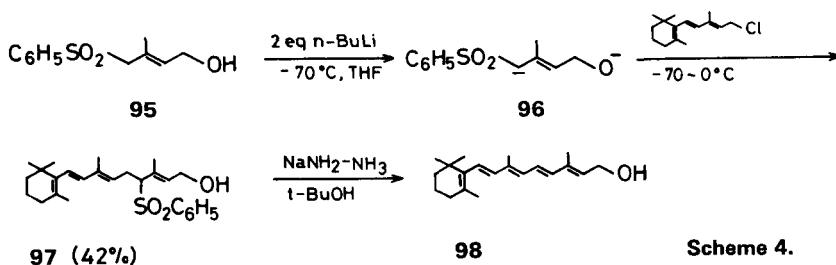
Scheme 4.

Another useful technique for the synthesis of Vitamin A has been reported by Torii *et al.*[72]

$$C_6H_5SO_2 \diagup\diagdown\diagup OH \xrightarrow[-78°C]{2\,eq\,LDA} C_6H_5SO_2 \diagup\diagdown\diagup O^- \xrightarrow[-78°C,\ 30\,min]{Br\diagup\diagdown COOCH_3}$$

$$HO\diagup\diagdown\underset{SO_2C_6H_5}{\diagup}\diagdown COOCH_3 \xrightarrow[\substack{2)\ \diagup\diagdown-CH_2SO_2Ph \\ 3)\ LDA \\ 4)\ t-BuOK}]{1)\ PBr_3} 98$$

$$92\,\%$$
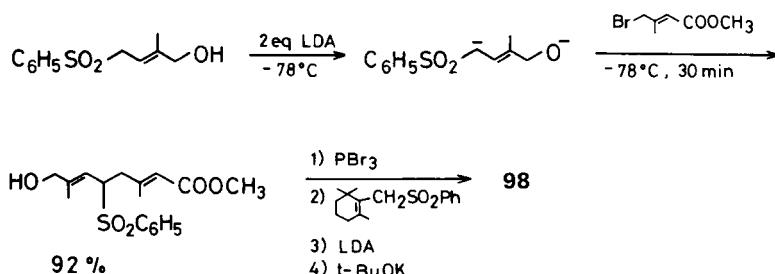
These results indicate that sulfone-stabilized allylic carbanions can be alkylated regioselectively α to the sulfone moiety.

The dianion of the α-alkoxy sulfone **100** can be generated by treatment with 2.2 equivalents of lithium diisopropylamide in THF with HMPA as a cosolvent.

$$C_6H_5SO_2CH_2O\diagup\diagdown O \xrightarrow[-78°C]{\substack{2.2\,eq\,LDA \\ THF-HMPA}} C_6H_5SO_2 \overset{Li}{\underset{\overset{|}{C}-O}{\diagup}}\diagdown O$$

100   **101**
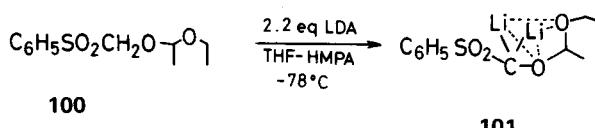
The alkylation of the dianion **101** with alkyl halides and subsequent aqueous hydrolysis give ketones in moderate yields (Table XVII).[73]

$$\textbf{101} \xrightarrow[THF-HMPA]{2\,eq\,RX} C_6H_5SO_2\overset{R}{\underset{R}{\overset{|}{C}}}-O\diagup\diagdown O \xrightarrow[2)\,OH^-]{1)\,H^+} \underset{O}{RCR}$$
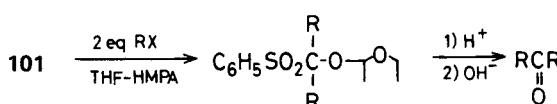
TABLE XVII

Synthesis of Ketones from Dianion 101 and Alkyl Halides

Alkyl halide	Ketone	Yield(%)
$n-C_4H_9Br$	$(n-C_4H_9)_2C=O$	52
$n-C_7H_{15}Br$	$(n-C_7H_{15})_2C=O$	72
$Br(CH_2)_5Br$	⬡=O	70
$n-C_{10}H_{21}Br$	$(n-C_{10}H_{21})_2C=O$	72
$n-C_6H_{13}Br$	$(n-C_6H_{13})_2C=O$	55

Therefore, the dianion **101** serves as a carbonyl dianion equivalent.[3]

$$C_6H_5SO_2-\overset{-}{C}-O\diagup\diagdown O \equiv \underset{O}{\overset{\overset{-}{C}^-}{\|}}$$

101
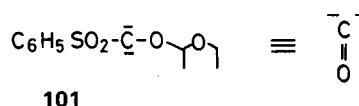
An efficient procedure for the synthesis of 1,2-disubstituted cyclopentenones has recently been developed by Fuchs and coworkers.[74] Treatment of the β-epoxy sulfone **102** with an organolithium reagent gives the dilithiated derivative which can be trapped with an alkyl halide to afford the γ-hydroxy sulfone **104**.
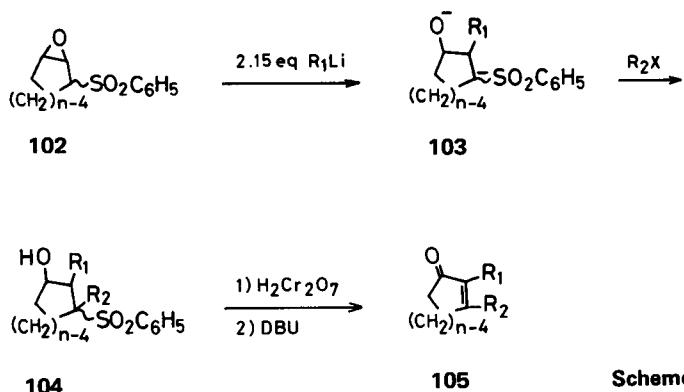
Scheme 5.

Conversion of **104** to enones is illustrated in Scheme 5.

TABLE XVIII

Synthesis of Cyclopentanone 104

Epoxy sulfone 102	R_1	R_2	Overall yield 105(%)
n = 5	C_6H_5	CH_3	89
	C_6H_5	$CH_2=CH-CH_2$	70
n = 6	C_6H_5	H	45
	$n-C_4H_9$	CH_3	44
n = 7	C_6H_5	CH_3	70
	$n-C_4H_9$	CH_3	46

The β-epoxy sulfone **102** can be regarded as the ynone synthon **106**.
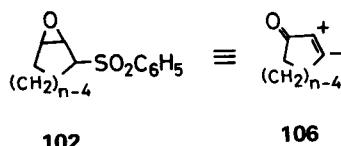
The reaction of ketone tosylhydrazones with organolithium reagents constitutes a useful synthetic route to olefins.[75,76] The mechanism proposed for the formation of olefin is considered to involve initially the tosylhydrazone dianions **108** which, by loss of arenesulfinate anion, give the vinyl anions **109** as shown in Scheme 6.
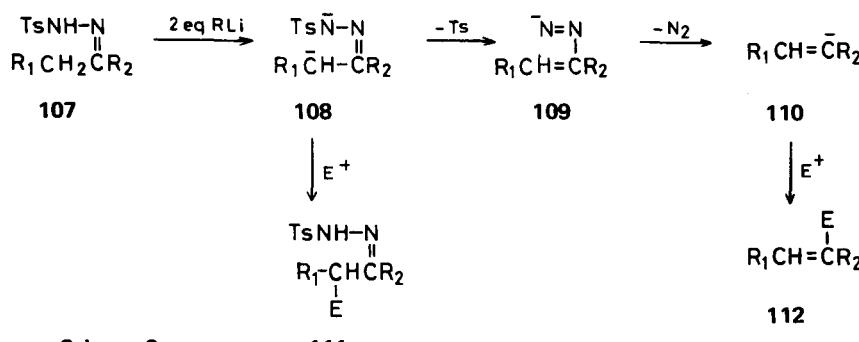
Scheme 6.

At $-78°C$, the dianion **108** can be trapped with a variety of electrophilic reagents to give the tosylhydrazone derivatives **111**.[77]
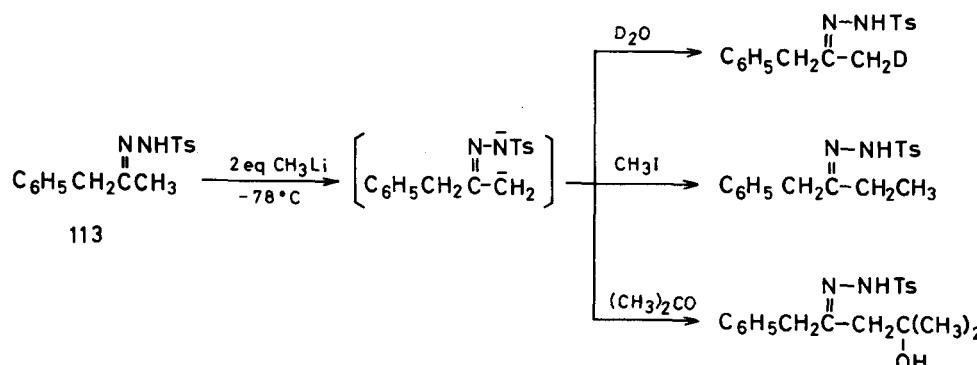
At higher temperatures, the tosylhydrazone dianions **108** decompose to afford the synthetically useful vinyl anions **110** which can also be trapped with electrophiles. Reactions involving the anions **110** are summarized in Table XIX.

The ready availability of tosylhydrazones makes these methods highly advantageous for the synthesis of a variety of olefins. The choice of the proper solvent and organolithium reagent is important in the case of the tosylhydrazones **114** and **115** (Table XX).[86]
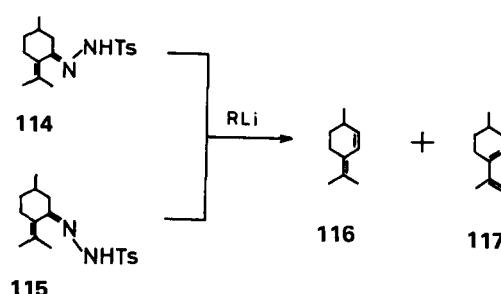
TABLE XIX

Syntheses of Fuctionally Substituted Olefins from Ketone Tosylhydrazones
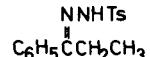
Reactant	Base	Solvent	Electrophile	Product	Yield (%)	Ref.
$C_6H_5\overset{NNHTs}{\underset{\parallel}{C}}CH_2CH_3$	2 eq n–BuLi	Benzene–TMEDA	CH_3I	$C_6H_5\overset{CH_3}{\underset{\mid}{C}}{=}CHCH_3$	95	77
[cyclohexane]=NNHTs	n–BuLi	Hexane–TMEDA	$n\text{–}C_3H_7Br$	[cyclohexane]–$n\text{–}C_3H_7$	67	77
[chain]=NNHTs	3.5 eq n–BuLi	TMEDA	C_6H_5CHO	$C_6H_5\overset{HO}{\underset{\mid}{C}}H{-}\overset{CH_2}{\underset{\parallel}{C}}C_6H_{13}$	78	78
			CO_2	$CH_2{=}\overset{COOH}{\underset{\mid}{C}}{-}C_6H_{13}$	52	78
			$n\text{–}BuBr$	$CH_2{=}\overset{C_4H_9}{\underset{\mid}{C}}{-}C_6H_{13}$	65	78
[structure]=NNHTs	4 eq n–BuLi	TMEDA	$HCON(CH_3)_2$	[structure]–CHO	60	79
[cyclohexene]–NNHTs	4 eq n–BuLi	TMEDA	$HCON(CH_3)_2$	[cyclohexene]–CHO	54	79
[chain]=NNHTs	4 eq n–BuLi	TMEDA	D_2O	[chain with D]	91	80
[pinane]–NNHTs	4 eq n–BuLi	TMEDA	D_2O	[pinane]–D	95	80
$C_6H_5\overset{NNHTs}{\underset{\parallel}{C}}CH_3$	4 eq n–BuLi	TMEDA	D_2O	$C_6H_5\overset{D}{\underset{\mid}{C}}{=}CH_2$	90	80
[cycloheptane]=NNHTs	4 eq n–BuLi	TMEDA	$(CH_3)_3SiCl$	[cycloheptene]–$Si(CH_3)_3$	62	81
[cycloheptane]=NNHTs	4 eq n–BuLi	TMEDA	$(CH_3)_3GeCl$	[cycloheptene]–$Ge(CH_3)_3$	64	81
[cycloheptane]=NNHTs	4 eq n–BuLi	TMEDA	$(CH_3)_3SnCl$	[cycloheptene]–$Sn(CH_3)_3$	56	81
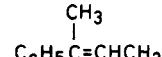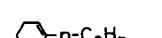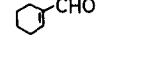
(Continued)

TABLE XIX CONTINUED
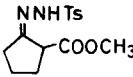
Reactant	Base	Solvent	Electrophile	Product	Yield (%)	Ref.
(cyclopentane) NNHTs, –COOCH$_3$	3eq LDA	THF	C$_6$H$_5$CH$_2$Br	(cyclopentene) CH$_2$C$_6$H$_5$, COOCH$_3$	49	82
(cyclohexane) NNHTs, –COOCH$_3$	3eq LDA	THF	CH$_3$I	(cyclohexene) CH$_3$, COOEt	79	82
NNHSO$_2$Ar, CH$_3$CC$_6$H$_{13}$	2eq n–BuLi	Hexane–TMEDA	C$_6$H$_5$CHO	OH, C$_6$H$_5$CH–C$_6$H$_{13}$	62	83
	2eq n–BuLi	Hexane–TMEDA	n–C$_4$H$_9$Br	C$_3$H$_7$CH$_2$–C$_6$H$_{13}$	58	83
	2eq n–BuLi	Hexane–TMEDA	BrCH$_2$CH$_2$Br	Br–C$_6$H$_{13}$	43	83
	2eq n–BuLi	Hexane–TMEDA	(CH$_3$)$_3$SiCl	(CH$_3$)$_3$Si–C$_6$H$_{13}$	71	83
NNHSO$_2$Ar, CH$_3$CCH$_3$	2eq s–BuLi	THF	1) n–C$_5$H$_{11}$I 2) CH$_3$CH$_2$I	CH$_3$CH$_2$, H; CH$_3$, n–C$_5$H$_{11}$	47	84
	2eq s–BuLi	THF	1) n–C$_5$H$_{11}$I 2) CH$_2$O	HOCH$_2$, H; CH$_3$, n–C$_5$H$_{11}$	52	84
	2eq s–BuLi	THF	1) n–C$_5$H$_{11}$I 2) HCON(CH$_3$)$_2$	OHC, H; CH$_3$, n–C$_5$H$_{11}$	56	84
CH$_3$O–⬡–CCHSCH$_3$, NNHTs, CH$_3$	6eq CH$_3$Li	Ether	CH$_3$I	CH$_3$O–⬡–C≡C–CH$_3$	53	85
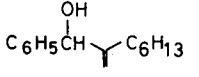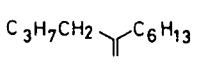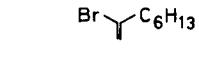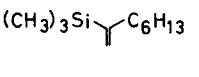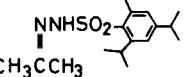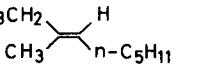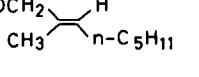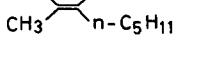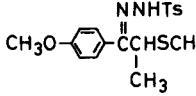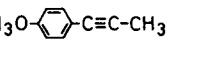
TABLE XX

Effect of Solvent and RLi

Reactant	RLi	Solvent	Product
114	CH$_3$Li	Benzene–Ether	116
115	CH$_3$Li	Benzene–Ether	116
114	n–BuLi	TMEDA	116
115	n–BuLi	TMEDA	116(10%) + 117(90%)
114	CH$_3$Li	THF	116(80%) + 117(20%)
115	CH$_3$Li	THF	116(20%) + 117(80%)

An attractive procedure for the regioselective synthesis of the homoallylic alcohols 119 from carbonyl compounds involves the elimination reaction of 118 which can be obtained from tosylhydrazone dianions and carbonyl compounds.[87]

118   **119 (48%)**
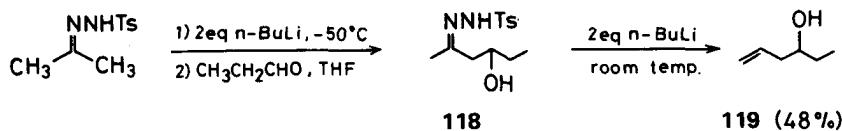
The alkylation of a dimetalated (E)-S-ethyl-S-methyl tosylhydrazone proceeds with a high regioselectivity at the α-carbon to give the syn-methylated product 121 in high yield.[88]

120

121 (91%)
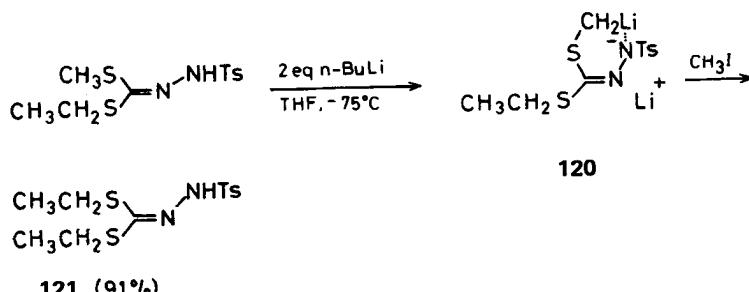
The direction of metalation is considered to be controlled by the six-membered ring chelation in 120. A useful route to 1,2-carbonyl transpositions is based upon the α-sulfenylation of tosylhydrazone dianions as illustrated by the conversion 122→123.[89]

122   **92%**   **123 (82%)**
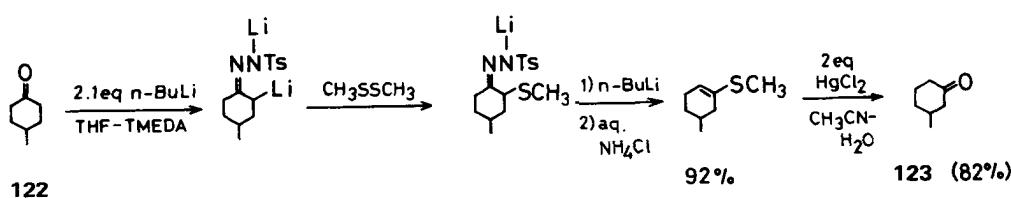
Another useful procedure for the synthesis of α-methylene-γ-butyrolactones has recently been developed. Treatment of β-hydroxy tosylhydrazones with n-butyllithium followed by carboxylation and cyclization gives lactones in good yields.[90,91]

124
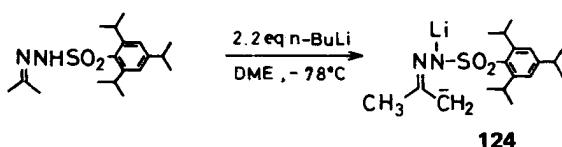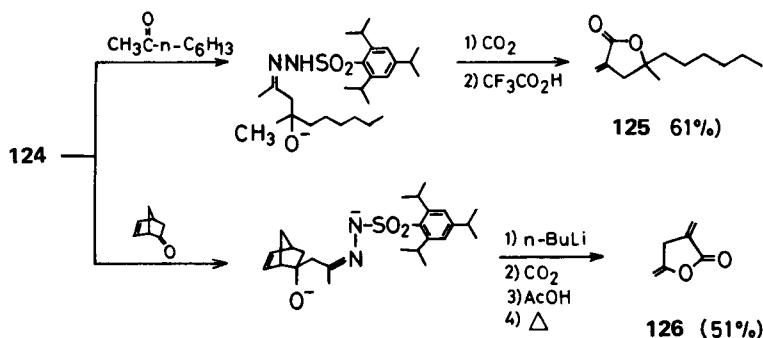
Attempts to generate the dianions of aldehyde tosylhydrazones 127 were fruitless. However, alkyllithium reagents add to aldehyde tosylhydrazones to give dimetalated species which on warming afford the alkanes 129 in moderate yields.[92]

$$R_1CH=NNHTs \xrightarrow{2\,eq\,R_2Li} R_1R_2CH\overset{\overset{Li}{|}}{\underset{}{N}}\overset{\overset{Li}{|}}{\underset{}{N}}Ts \xrightarrow{H_2O} R_1R_2CH_2$$

<div style="text-align:center">127   128   129</div>
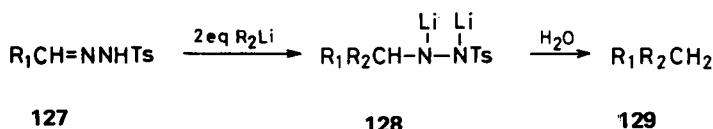
Several examples are shown in Scheme 7.
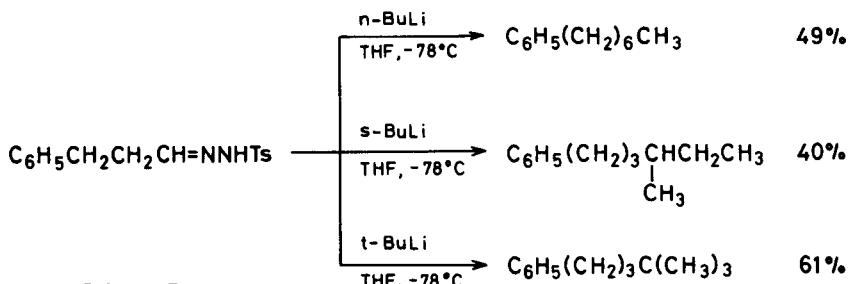
Scheme 7.

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