

REARRANGEMENTS OF THE CARBANIONS DERIVED FROM ALLYL BENZYL THIOETHER

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Abstract—The metalation of allyl benzyl thioether involves the benzylic or the allylic hydrogens. The benzylic carbanion undergoes a rapid [2,3] sigmatropic shift whereas the allylic carbanion gives rise to various rearrangements, among them migration of the allylic unit to the *para* position with allylic inversion. The temperature dependence of the ratio of products arising from the benzylic carbanion vs those from the allylic carbanion shows that the allylic-to-benzylic carbanion transformation occurs only under special conditions: (a) with slow addition of the base; (b) with thioether in excess relative to the base, and (c) on raising the temperature of the reaction medium from -78° to -15° . In the last instance, the proton transfer is intramolecular as shown with labeled thioethers. The extent of the different rearrangements depends on the temperature and solvent. A choice of mechanism cannot be made at this time for the *para* migration $5 \rightarrow 9a$. A leaving group effect on the reaction regioselectivity of the carbanion from allyl methyl thioether with benzyl halides has been noticed. The presence of dibenzyl indicates that, in addition to S_N2 reactions, some electron transfer process is occurring.

Carbanions derived from benzylallyl ethers and thioethers undergo different rearrangements depending on the position of metalation. If the benzylic position is metalated, [2,3] and [1,2] sigmatropic shifts of the allyl group are observed.^{1,2} However, if the allylic position is involved, [1,2] and [2,3] shifts and more complicated processes are detected. For instance, the allyl (α -phenyl ethyl) ether 1 gives, after reaction with methyl lithium, the three carbinols 2, 3 and 4.^{1b} Similarly, we previously described the reactions of allyl benzyl thioether and of benzyl γ,γ -dimethyl allyl thioether 31.²

For the benzyl γ,γ -dimethyl allyl thioether, the product of sigmatropic shift of the benzylic carbanion was obtained in high yield. Metalation at both the benzylic and allylic positions in allyl benzyl thioether 5 was observed. The benzylic carbanion 13 rapidly undergoes a [2,3] sigmatropic shift, whereas the allylic carbanion 14

reasonably stable at -78° , undergoes several rearrangements at higher temperatures leading to products 9a, 10a and 11.² The change in the ratio of the products derived from allylic vs benzylic metalation with temperature was intriguing. The migration of the allylic unit with allylic inversion to the *para* position was felt to be worthy of the further investigation reported here. Minor products were isolated and their structure established.

The structures of products 6, 7, 8 and 11 were ascertained by NMR.

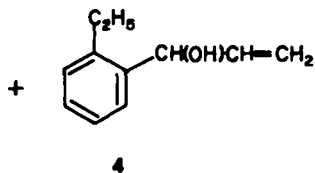
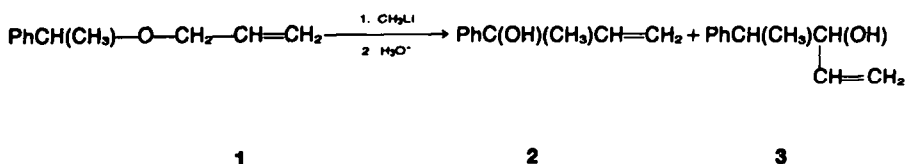
The vinylic thioethers 9a, 10a and 10b were prepared according to the following reaction scheme.† The *E* isomers 9a and 10a were obtained in 35% and 27% yield, respectively, and the *Z* isomers 9b and 10b in 25% and 27% yield. The stereochemistry was established by NMR, the coupling constant of the vinylic protons being 15 Hz for 9a and 10a and 9 Hz for isomers 9b and 10b. Compounds 9a and 10a were identical with the corresponding rearrangement products. The *Z* isomer 9b is not present in detectable amount among the rearrangement products. However, the *Z* isomer 10b was identical with one of the minor products. It thus appears that migration to the *para*-position gives only the *E* isomer.

The structure of another minor product was suggested to be 12. Product 12 was prepared by reaction of the allyl methyl thioether anion with benzyl halides. With benzyl

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‡In the initial work,² thioethers 9a and 10a were degraded by ozonolysis and subsequent reduction to known alcohols.



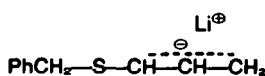
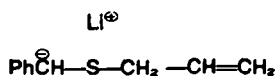
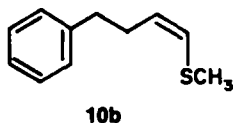
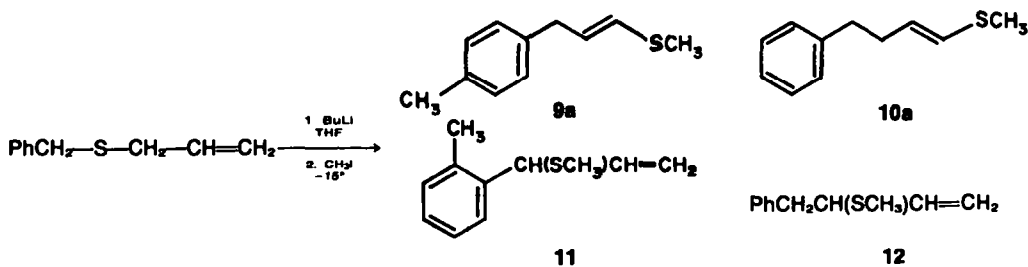
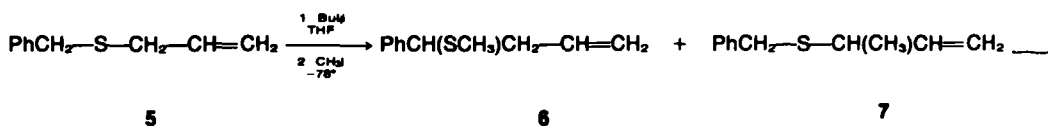


Table 1.

T°	<u>6</u>	<u>7</u>	<u>8</u>	<u>9a</u>	<u>10a</u>	<u>11</u>	<u>12</u>	<u>10b</u>
-78°C	23%	76%	1%	-	-	-	-	-
-15°C	65%	-	-	25%	5%	4%	c	c

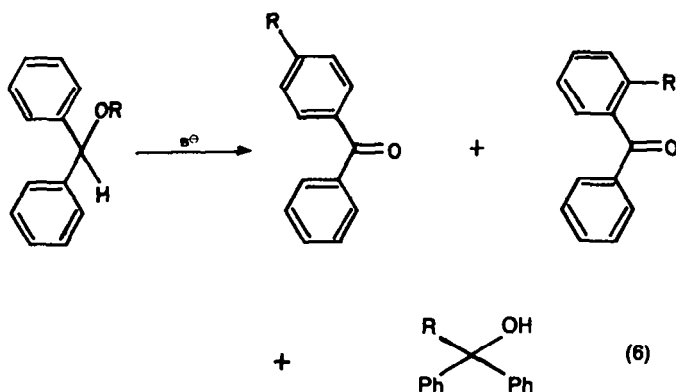
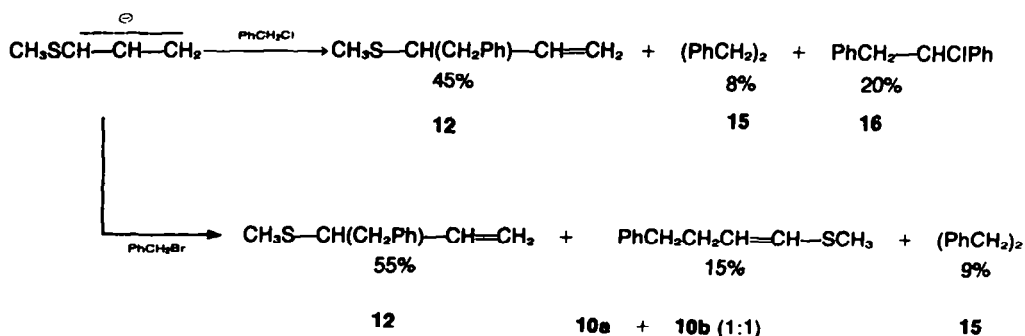
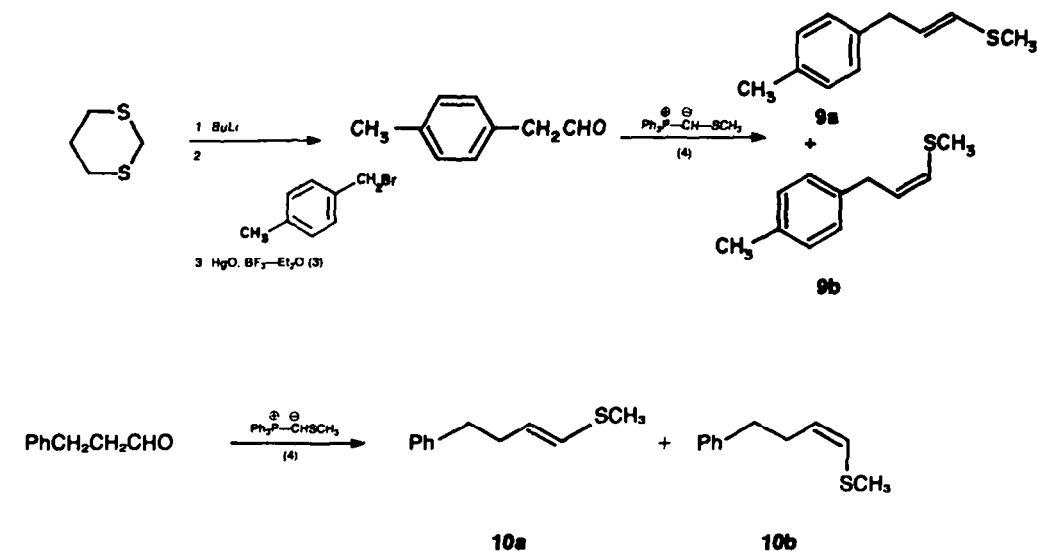
chloride, authentic α -alkylated product 12, identical with the minor rearrangement product, was obtained. The two bibenzyl products 15 and 16 were also produced. If benzyl bromide was used, however, α and γ alkylated products as well as bibenzyl 15 were isolated. This effect of the leaving group on the reaction regioselectivity has been previously noticed.⁵ The presence of benzylic coupling products in the case of the chloride suggests the occurrence of a reaction pathway other than a simple S_N2 reaction of the carbanion with the halide.

The structure of the reaction products being firmly established, two puzzling observations remained. Firstly, the ratio of the products arising from the allylic carbanion to those from the benzylic carbanion changed with the reaction conditions. The ratio of benzylic/allylic product (6/7 and 8) or 6/9a, 10a, 11, 12 and 10b) was 1/3 at -78° and 3/1 at the other temperatures (-40°; -15°; -78° (0.5 hr) -15°). Is there a prototropic shift which equilibrates both anions?

Secondly, the migration of an allylic moiety to the *para* position of a benzene ring has been reported to occur in low yields in some other reactions.⁶ However, it should be noticed that in the migration discussed here the anionic allylic unit is the migrating fragment, whereas in the cited example⁶ the migration occurs to the *para* position of a benzylic anion.

In order to gain some insight on these two points, we studied the reaction as a function of the temperature and of the reaction medium, as well as by isotopic labeling techniques.

In first place, we established that the ratio benzylic/allylic products did not depend on the time the carbanion was left at -78°. If methyl iodide was added 5 min or 1 hr after butyllithium, the ratio 6/7 and 8) remained the same. Thus the allylic carbanion was not transformed into the benzylic carbanion which undergoes a rapid [2, 3] sigmatropic shift. However, it was found that if a stoichiometric quantity of butyllithium was added over a



period of 2 hr, or if half of the stoichiometric amount of base was rapidly added, only one reaction product 6 was isolated in addition to starting material. These experiments show that intramolecular proton shift is quite slow at -78° (reaction 1), but that intermolecular proton shift may occur under certain reaction conditions† (reaction 2).

†Isomerisation of allyl methyl phenylamine to methyl phenyl propenyl amine occurred when the base was added slowly. If the base was added rapidly, the allylic carbanion was produced.^{14a} An intramolecular 1,4 proton transfer has been observed for the 5-hexenyl anion.^{14b}

For a better understanding of the reactions occurring at higher temperature, we prepared the deuterium labelled (1,1-²H₂ benzyl) allyl thioether 17 and studied its behaviour under different reaction conditions.

When metalated and treated at -78° with methyl iodide, the products 18, 19 and 20 were obtained in a ratio different from that observed with 5→6, 7 and 8. Product 18, originating from the benzylic carbanions, was obtained in a yield of 5% and was monodeuterated. This confirms the absence of intra and intermolecular hydrogen migration at -78° when a 1,1 equivalent of *n*-butyllithium is added rapidly. The C-methylated products 19 and 20 were dideuterated. The primary iso-

Table 2.

Temperature	<u>18</u>	<u>19</u>	<u>20</u>	<u>21</u>	<u>22</u>	<u>23</u>	<u>24</u> E + Z
-15°C	29%	-	-	38%	15%	3%	ε
(a)	D ₀ : 3%			0%	0%	0%	0%
	D ₁ : 95%			2%	2%	2%	2%
	D ₂ : 2%			98%	98%	98%	98%
-78°C and -15°C	7-8%	-	-	68%	20%	ε	2%
(b)	D ₀ : 2%			0%	0%	0%	0%
	D ₁ : 91%			2%	2%	2%	2%
	D ₂ : 7%			98%	98%	98%	98%

(a) metalation, rearrangement and reaction with methyl iodide performed at -15°C

(b) addition of butyllithium at -78°C, temperature increased to -15°C, methyl iodide added at -15°C.

(3/1) is attributable to the change in kinetic acidity of the benzylic vs allylic protons with temperature changes and not to the occurrence of a proton shift.

In order to improve the yield of product **9a** resulting from migration to the *para* position, we examined the effect of variations in the reaction medium and temperature. The results are presented in Table 3.

The isotope effect observed with benzyldideuterated thioether **17** favors the formation of the allylic carbanion, which is advantageous for this study. Some results on this system are presented in Table 4. The *para* migration is favored by temperatures higher than -40° and by solvating media.

In order to explore the generality of the migration to

Table 3.

	<u>6</u> ^{a)}	<u>7</u> ^{b)}	<u>8</u> ^{b)}	<u>9a</u> ^{b)}	<u>10a</u> ^{b)}	<u>11</u> ^{b)}	<u>12</u> ^{b)}	<u>10b</u> ^{b)}
-78°C THF/TMEDA	23%	98.7	1.3	-	-	-	-	-
-78°C and -15°C THF/TMEDA	65%	-	-	81	15	-	1.5	1.5
-15°C THF/TMEDA	65%	-	-	69.5	14	11	2.5	2.5
-78°C THF/TMEDA HMPT	55%	55	1	21	21	-	0.5	0.5
-78°C and -15°C THF/TMEDA HMPT	62%	-	-	59	40.5	-	-	0.5
-15°C THF/TMEDA HMPT	73%	-	-	81.5	18	0.5	-	-

a) These yields are calculated with respect to the total amount of allyl benzyl thioether **5**.

b) These products arise from the allylic carbanion of thioether **5**, after alkylation with methyl iodide. The numbers given are yields calculated with respect only to the allylic carbanion.

Table 4.

	<u>18</u> ^{a)}	<u>19</u> ^{b)}	<u>20</u> ^{b)}	<u>21</u> ^{b)}	<u>24E</u> ^{b)}	<u>22</u> ^{b)}	<u>23</u> ^{b)}	<u>24Z</u> ^{b)}
-78°C THF/TMEDA	5%	96.5	3.5	-	-	-	-	-
-78°C and -15°C THF/TMEDA	7-8%	-	-	75.5	1	22	-	1
-15°C THF/TMEDA	29%	-	-	66.5	0.5	26.5	5	0.5
-15°C THF/TMEDA HMPT	24%	-	-	88.5	-	10.5	0.5	-

a) The yields are calculated with respect to the total amount of allyl(1,1-²H₂)benzyl thioether 17.

b) These products arise from the allylic carbanion of thioether 17, after alkylation with methyl iodide. The numbers given are yields calculated with respect only to the allylic carbanion.

the *para* position, we studied the behaviour of thioether 25, in which the metalation should be more regioselective than in allyl benzyl thioether 5. The H atom on the tertiary carbon α to the aromatic ring should be less acidic than the allylic hydrogens. Indeed, at -78°, the carbanion was stable in tetrahydrofuran and yielded products corresponding to methylation of the allylic carbanion in a yield of 96%, of which 92% was the product alkylated in the α position and the remaining 4% in the γ position.

The results of studies at higher temperatures and with different media are summarised in Table 5. The structures of products 28 and 29 were ascertained by synthesis.

The highest yield of *para* rearranged product 30 was 30%. Some of the results obtained here contradict those obtained with allyl benzyl thioether 5. For instance, the amount of the *para* rearranged product with respect only

to the allylic carbanion (9a and 30, respectively) is always greater for thioether 5 than for thioether 25, whereas the percentage of thioether resulting from a Stevens type rearrangement (12 and 28, respectively) is less important for 5 than for 25. Moreover, no *ortho* migration product was found among the reaction products of thioether 25.

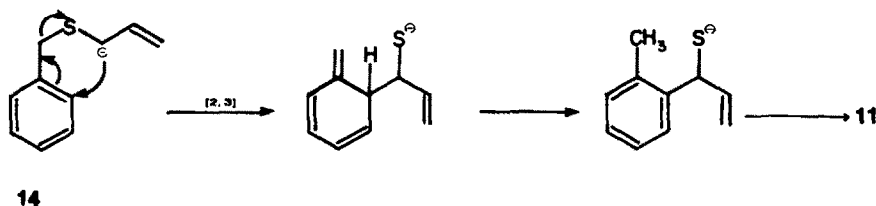
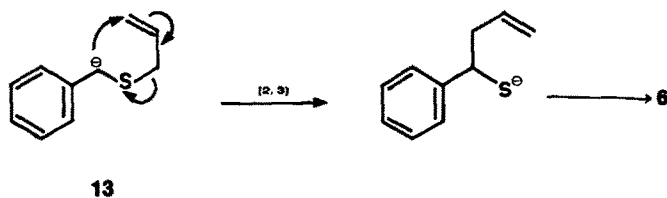
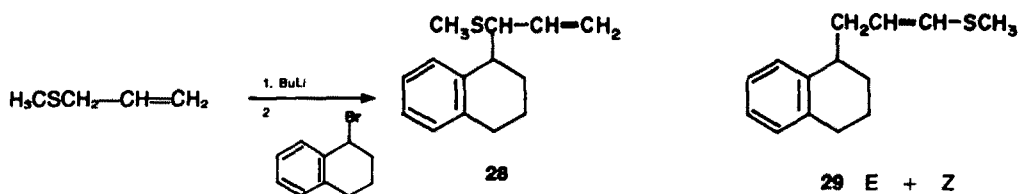
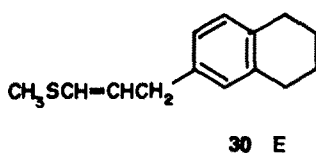
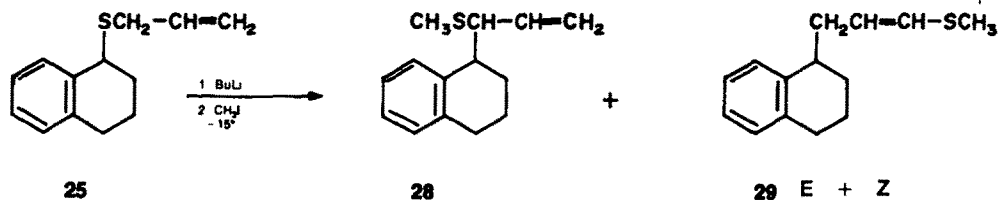
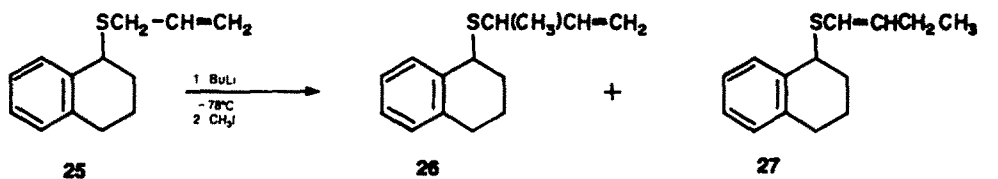
Due to the multiplicity of reaction products, we did not carry out further mechanistic studies of these rearrangements.

The rearrangement of the benzylic carbanion from allyl benzyl thioether is a classical [2,3] sigmatropic shift, of which numerous examples have been described both for carbanions and for ylides.^{1,2,11} This sigmatropic shift could be concerted.

The migration of the allylic carbanion to the *ortho* position is an example of a [2,3] sigmatropic shift, of which several examples are also known.^{1b,1c,12}

Table 5.

	<u>26</u>	<u>27</u>	<u>28</u>	<u>29</u>	<u>30</u>
-78°C THF/TMEDA	92%	4%	-	-	-
-15°C THF/TMEDA	-	-	35%	35%	8%
				Z:E 1/3	
-78°C and -15°C THF/TMEDA	-	-	10%	12%	30%
				Z:E 1/5	
-15°C THF/TMEDA HMPT	-	-	18%	18%	18%
				Z:E 1/5	



Allylic carbanion **14** may also undergo dissociation to a free radical and a radical anion, a mechanism proposed for the transposition of some ylides and carbanions.^{6,12} In view of the stereochemistry of the double bond in **10a** and **10b**, the radical anion undergoes equilibration, or the carbanion exists as *E* and *Z* isomers.

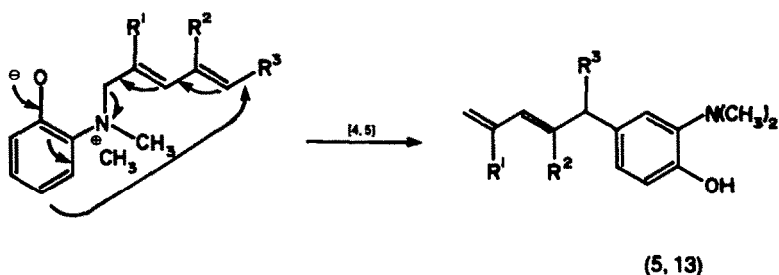
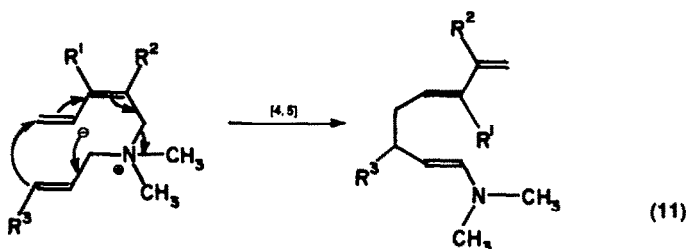
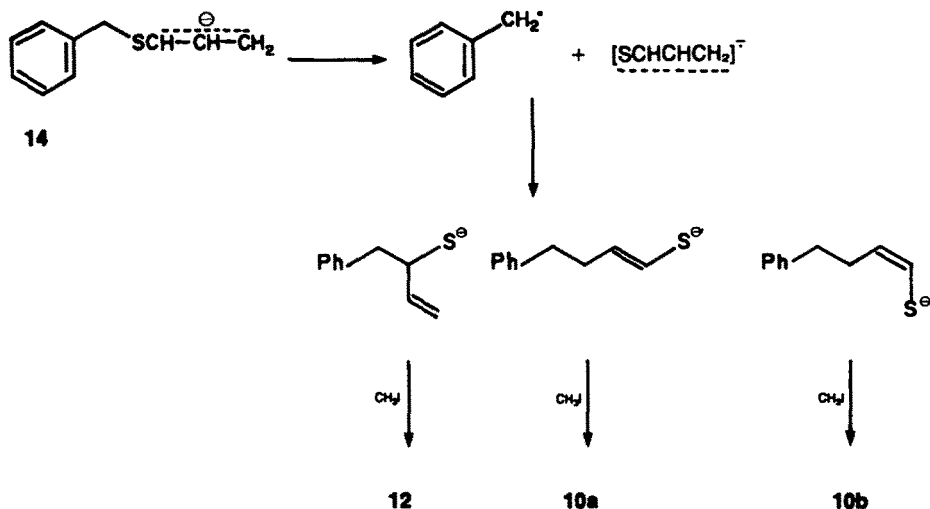
For the *para* migration several explanations can be proposed:

(a) A [4,5] sigmatropic shift. This would explain why only the *E* product **9a** was isolated. Some examples of such migrations have been described for ylides (Fig. 13).^{4,11,13}

(b) Another possibility is the occurrence of two suc-

cessive migrations, a [2,3] followed by a [3,3] sigmatropic shift. However, it is unlikely that the [3,3] sigmatropic shift is more rapid than the proton shift. Not much energy should be gained starting from allylic thiolate and ending with a vinylic thiolate. There seems to be very little delocalisation of the charge at the sulfur into the double bond. Moreover, from consideration of molecular models, it is not quite clear why only the *E* product **9a** would be obtained.

(c) The third possibility is the dissociative mechanism. But this does not at first explain why only the *E* product is obtained. As required by the isolation of *E* and *Z* isomers **10a** and **10b**, the *E* and *Z* carbanion precursors



must exist in solution. Alternatively, an intermediate whose isomerisation is quite fast with respect to the other reactions may intervene in the reaction leading to 9 and 10. The occurrence of this dissociative mechanism can be tested.

The reaction of benzophenone dianion with allyl iodides involves some electron transfer.⁶ In the reaction of the dianion of allyl thiol¹⁵ with some halogenides, an electron transfer pathway is detected by the formation of bibenzyl (Table 6).† However no product substituted in the *para* position was detected. Thus the *para* migration discussed above does not involve free radicals as intermediates, or different free radicals are formed which then evolve in different modes.

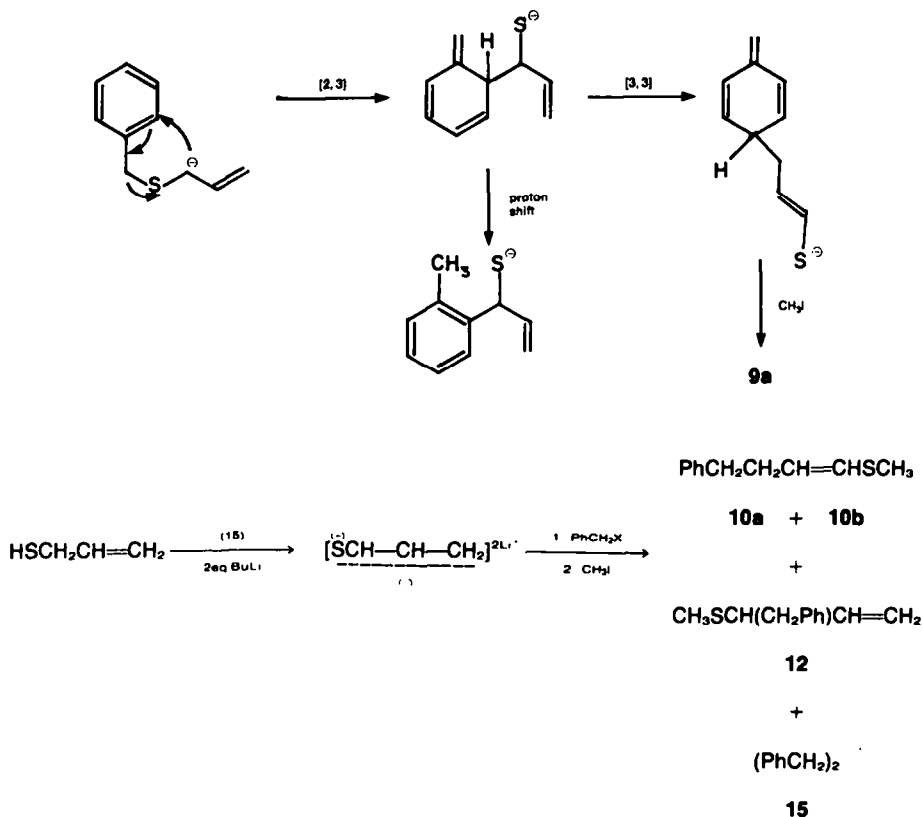
In conclusions, the rearrangements of the carbanions derived from allyl benzyl thioether raise several ques-

Table 6.

x	10b	10a	12	15	16
Br	50%	4%	18%	18%	-
Cl	50%	4%	11%	17%	8%

tions. The temperature dependence of the kinetic acidity of allylic vs benzylic hydrogen is very puzzling. Under some conditions, a [1,3] intramolecular proton shift occurs, although for the carbanion from allyl benzyl thioether, this shift is slow compared to the other rearrangements. The *para* migration 13 to 9a seems to be quite unique. No firm preference for a mechanism is available. The multiplicity of the rearrangements occurring simultaneously complicates the kinetic study, which for this reason was not undertaken. Further investigations, however, may lead to the discovery of systems where the *para* migration is the major if not the

† In this reaction the *E* product 10a was found in trace amount. This is in contrast to what has been described earlier where only the *Z* products were isolated.¹⁵



single process. In conclusion, the rearrangements of the carbanions from allyl benzyl thioether are as complex as those observed with some carbocation.

EXPERIMENTAL

The ^1H NMR spectra were determined at 60 MHz on a Varian A 60 or Perkin-Elmer R 12 spectrometer. The solvent (except where otherwise indicated) was CCl_4 . The chemical shifts are reported in ppm relative to internal TMS. The IR spectra were recorded on a Perkin-Elmer IR-177 spectrometer. Mass spectra (MS) were obtained on a Thomson Houston THN 208 or LKB 900 S mass spectrometer. Preparative glc separations were performed on a Varian Aerograph autoprep model 700 instrument equipped with a catharometer.

A commercially available solution of BuLi in hexane, about 2 M, was used.¹⁶ A N_2 or argon atmosphere was employed in all reactions involving Li compounds.

Reaction of benzyl γ,γ -dimethyl allyl thioether

A soln of thioether (1.73 g) in THF (50 ml) with 1.2 eq. of diazabicyclo [2, 2, 2] octane was treated at -15° with BuLi (1.1 eq). After 1 hr, MeI (1.2 eq), then water was added and extraction was performed with ether. 1-Methylthio-1-phenyl-2,2-dimethylbut-3-ene (1.8 g) was thus obtained in a yield of 96.5%.

1-Methylthio-1-phenyl-2,2-dimethylbut-3-ene. ^1H NMR: δ = 1.02 (s, 3H), 1.09 ppm (s, 3H), 1.69 ppm (s, 3H), 3.41 ppm (s, 1H), 4.91 ppm (q, J = 11 Hz; J = 1.5 Hz; 1H), 4.83 ppm (q, J = 16.5 Hz; J = 1.5 Hz; 1H), 5.93 ppm (q, J = 11 Hz, J = 16.5 Hz, 1H), 7.17 ppm (5H). MS: M^+ 206. (Found: C, 75.8; H, 8.8. Calc. for $\text{C}_{13}\text{H}_{18}\text{S}$: C, 75.66; H, 8.80%.)

Metalation of allyl benzyl thioether at -78° ^{5d}

An 0.15 M soln of **5** and tetramethylethylenediamine (1.2 eq) in THF was cooled to -78° . A 1.1 eq of BuLi in hexane was added slowly. After 0.5 hr, an excess of MeI was added. After addition of water and ether, the ether layer was washed with water and dried over Na_2SO_4 . After evaporation, the mixture of products was analysed by ^1H NMR, analytical glc using reference samples

(OV 17 3% at 130°), and sometimes separated by silica gel chromatography (eluent petrol ether: benzene 98:2) or preparative glc.

For the experiments at different temps and reaction times and in different media, the metalation of **5** was carried out as above at the indicated temp, in the specific solvent, and the alkylating agent added after the given time. The results are summarised in Tables 1 and 3.

Metalation of allyl benzyl thioether 5 at -78° and methylation at -15° . The same procedure as for **5** at -78° was used except that MeI was added at -15° , after 0.5 hr. Product ratios indicated in Table 3.

Metalation of allyl benzyl thioether 5 at -78° by 0.5 eq of n-BuLi. The same procedure as for **5** at -78° was used except that the metalation was done with 0.5 eq of BuLi. Excess of MeI was added after 0.5 hr at -78° . Product ratios are indicated in Table 1.

Metalation of allyl benzyl thioether 5 at -78° by 1 eq of n-BuLi added dropwise. The same procedure as for **5** at -78° was used except that the 1 eq BuLi was added dropwise over a period of 2 hr. The product ratio is indicated in Table 1.

For compound 6. ^1H NMR: δ = 1.80 ppm (s, 3H); 2.55 ppm (t, J = 7.5 Hz, 2H); 3.53 ppm (t, J = 7.5 Hz, 1H); 4.73–6.03 ppm (m, 3H); 7.20 ppm (m, 5H); MS: M^+ 178 (Found: C, 74.2; H, 7.9. Calc. for $\text{C}_{11}\text{H}_{14}\text{S}$: C, 74.10; H, 7.91%).

For compound 7. ^1H NMR: δ = 1.25 ppm (d, J = 7 Hz, 3H); 3.10 ppm (q, J = 7 Hz, 1H); 3.55 ppm (s, 2H); 4.73–5.15 ppm (m, 2H); 5.37–6.02 ppm (m, 1H); 7.20 ppm (m, 5H).

For compound 8. ^1H NMR: δ = 0.98 ppm (t, J = 6.5 Hz, 3H); 2.00 ppm (m, J = 6.5 Hz, 2H); 3.76 ppm (s, 2H); 5.66 ppm (m, 2H); 7.20 ppm (m, 5H).

For compound 11. ^1H NMR: δ = 1.94 ppm (s, 3H); 2.33 ppm (s, 3H); 4.37 ppm (d, J = 7.5 Hz, 1H); 4.85–5.25 ppm (m, 2H); 5.68–6.20 ppm (m, 1H); 6.97–7.45 ppm (m, 4H).

Synthesis of cis and trans (methylthio)-1-p-tolyl-3 propene

Preparation of 2(4-methylbenzyl)1,3-dithiane. α -Bromo-p-xylene (1.025 g) was added at -10° , to a soln of 2-lithium-1,3-dithiane (prepared from 1,3-dithiane (0.600 g), 1.05 eq of BuLi

and tetramethylethylenediamine (0.85 ml), at -10° , in THF (30 ml).

After 1 hr, water then CHCl_3 were added, and the CHCl_3 layer was washed with water, brine and dried over Na_2SO_4 . After evaporation and chromatography on silica gel (80 g) (eluted with EtOAc-petrol ether 5/95), the product (0.950 g, 80%) was recrystallised from a mixture of diethylether and petrol ether.

M.p.: $71-72^\circ$; $^1\text{H NMR}$: $\delta = 1.75-2.15$ ppm (m, 2H); 2.30 ppm (s, 3H); 2.65-2.90 ppm (m, 4H); 2.88 ppm (d, $J = 7$ Hz, 2H); 4.07 ppm (t, $J = 7$ Hz, 1H); 7.01 ppm (s, 4H). MS: M^+ 224; base peak at m/e 119 (Found: C, 64.1; H, 7.2. Calc. for $\text{C}_{12}\text{H}_{16}\text{S}_2$: C, 64.17; H, 7.19%).

Synthesis of (*p*-methyl)phenylacetaldehyde (17). The hydrolysis of the preceding dithiane was done according to the lit.³ The expected aldehyde was isolated in a yield of 95%. $^1\text{H NMR}$: $\delta = 2.31$ ppm (s, 3H); 3.49 ppm (d, $J = 2$ Hz, 2H); 7.07 ppm (s, 4H); 9.60 ppm (t, $J = 2$ Hz, 1H). IR spectrum (CHCl_3) 1725 cm^{-1} $\nu_{\text{C=O}}$.

Synthesis of the vinylic thioethers 9*b* Z and 9*a* E. To a soln of triphenylmethylmercapto methylenephosphorane⁴ (1.3 mM) in THF (30 ml), (*p*-methyl)phenylacetaldehyde (0.45 mM, 0.060 g) was added. After 14 hr heating under reflux, the ppt was filtered off and washed with ether. After the usual extraction with ether and chromatography on silica gel with petrol ether/benzene 98/2, a mixture of Z and E isomers (0.050 g) (Z/E ratio: 1/1.3) was isolated. They were separated by preparative gas chromatography on OV 17 11% on chromosorb W 45/60 mesh at 170° .

For compound 9*b* Z. $^1\text{H NMR}$: $\delta = 2.25$ ppm (s, 3H); 2.28 ppm (s, 3H); 3.35 ppm (d, $J = 6$ Hz, 2H); 5.15-6.15 ppm (m, $J = 9$ Hz, 2H); 6.97 ppm (s, 4H).

For compound 9*a* E. $^1\text{H NMR}$: $\delta = 2.15$ ppm (s, 3H); 2.28 ppm (s, 3H); 3.35 ppm (d, $J = 6$ Hz, 2H); 5.15-6.15 ppm (m, $J = 15$ Hz, 2H); 6.97 ppm (s, 4H).

Synthesis of vinylic thioethers 10*a* E and 10*b* Z. The same procedure as for 9 (Z and E) was used here. The two isomers (Z/E ratio: 1/1) were isolated in a yield of 55%. They were separated by gas chromatography on OV 17 11% Chromosorb W 45/60 at 170° .

For compound 10*b* Z. $^1\text{H NMR}$: $\delta = 2.16$ ppm (s, 3H); 2.24-2.97 ppm (m, 4H); 5.32-6.10 ppm (m, $J = 9$ Hz, 2H); 7.15 ppm (s, 5H).

For compound 10*a* E. $^1\text{H NMR}$: $\delta = 2.13$ ppm (s, 3H); 2.24-2.97 ppm (m, 4H); 5.32-6.10 ppm (m, $J = 15$ Hz, 2H); 7.15 ppm (s, 5H).

Metalation of methyl allyl thioether and alkylation with benzylbromide. To a soln of methyl allyl thioether (0.35 g) and tetramethylethylenediamine (0.7 ml) in THF (20 ml), at 0° , a soln of BuLi in hexane (1.05 eq) was added. After 0.5 hr at 0° , benzylbromide (0.53 ml) was added. Hydrolysis, extraction with CHCl_3 , and evaporation of the solvent yielded a colorless oil (0.70 g). By chromatography on silica gel with petrol ether/benzene 98:2 we isolated 15% of 10*a* and 10*b* (ratio: 1/1), 55% of 12 and 9% of 15.

For compound 12. $^1\text{H NMR}$: $\delta = 1.90$ ppm (s, 3H); 2.70-3.45 ppm (m, 3H); 4.64-5.15 ppm (m, 2H); 5.32-5.95 ppm (m, 1H); 7.18 ppm (s, 5H); MS: M^+ 178. Base peak at m/e 87 (Found: C, 74.3; H, 7.9. Calc. for $\text{C}_{11}\text{H}_{14}\text{S}_2$: C, 74.10; H, 7.91%).

Metalation of methyl allyl thioether and alkylation with benzyl chloride. The same procedure as above with benzyl bromide was used, except that benzyl chloride (1.10 eq) was added after 0.5 hr at 0° . Hydrolysis, extraction with CHCl_3 , and evaporation of the solvent yielded a colorless oil (0.60 g). By chromatography on silica gel with petrol ether/benzene 98:2, we isolated 45% of 12, 20% of 16 and 8% of 15.

Dimetalation of allyl mercaptan and alkylation with benzyl halide (1 eq) and methyl iodide. The dimetalation was done according to the lit.¹⁵ Either benzyl bromide (1 eq) or benzyl chloride (1 eq) were added first, followed by MeI. Extraction was done with ether. $^1\text{H NMR}$ data and analytical gic were used to determine the ratio of the different products. These were separated by chromatography on silica gel with petrol ether/benzene mixtures. The results are presented in Table 6.

Synthesis of allyl (1,1- $^2\text{H}_2$) benzylthioether 17. Dideuterated benzyl bromide (prepared from methyl benzoate by reduction

with lithium aluminium deuteride in ether, followed by reaction of the benzylic alcohol with PBr_3 in benzene) (17.5 g) was added, at 0° , to a soln of sodium alkylthiolate (prepared from allyl mercaptan (8.8 ml) and sodium methylate (1.1 eq) in MeOH (200 ml) at 20° ; the product was extracted with ether, and distilled under reduced pressure. The yield was 85%.

For compound 17. $^1\text{H NMR}$: $\delta = 2.93$ ppm (d, $J = 7$ Hz, 2H); 4.80-5.20 ppm (m, 2H); 5.45-6.00 ppm (m, 1H); 7.20 ppm (m, 5H). MS: M^+ 166; base peak at m/e 93. Deuterium content determined by MS: 98% D_2 , 2% D_1 (Found: C, 72.2; H, 7.7. Calc. for $\text{C}_{16}\text{H}_{10}\text{D}_2\text{S}_2$: C, 72.23; H, 6.06; D, 2.42%).

Metalation of allyl (1,1- $^2\text{H}_2$) benzylthioether 17 and methylation at -78° . To a soln of 17 (0.33 g) and tetramethylethylenediamine (0.37 ml) in THF (15 ml), at -78° , a soln of BuLi in hexane (1.1 eq) was added. The medium turned yellow. After 0.5 hr, MeI was added. The usual extraction with ether was done yielding after evaporation of the solvent a colorless oil (0.34 g). The mixture was separated by gas chromatography on SE 30 30% on chromosorb W at 130° .

For compound 19 92%. $^1\text{H NMR}$: $\delta = 1.25$ ppm (d, $J = 7$ Hz, 3H); 3.08 ppm (q, $J = 7$ Hz, 1H); 4.73-5.15 ppm (m, 2H); 5.38-6.02 ppm (m, 1H); 7.20 ppm (m, 5H). MS: M^+ 180; base peak at m/e 93. Deuterium content determined by MS analysis: 98% D_2 , 2% D_1 .

For compound 20 3%. $^1\text{H NMR}$: $\delta = 0.95$ ppm (t, $J = 7$ Hz, 3H); 2.10 ppm (m, 2H); 5.47-5.93 ppm (m, 2H); 7.30 ppm (m, 5H).

For compound 18 5%. $^1\text{H NMR}$: $\delta = 1.79$ ppm (s, 3H); 2.54 ppm (d, $J = 7$ Hz, 2H); 4.74-5.16 ppm (m, 2H); 5.36-5.95 ppm (m, 1H); 7.20 ppm (m, 5H). MS: M^+ 179; base peak at m/e 138. Deuterium content 95% D_1 , 5% D_2 .

Metalation of allyl (1,1- $^2\text{H}_2$) benzylthioether 17 and methylation at -15° . The same procedure was applied as above. Results are summarised in Table 2.

For compound 21. $^1\text{H NMR}$: $\delta = 2.15$ ppm (s) and 2.28 ppm (m, 4H); 3.32 ppm (d, $J = 6$ Hz, 2H); 5.30-6.12 ppm (m, $J = 15$ Hz, 2H); 6.98 ppm (s, 4H). MS: M^+ 180; base peak at m/e 133. Deuterium content: 98% D_2 , 2% D_1 .

For compound 22. $^1\text{H NMR}$: $\delta = 1.94$ ppm (s, 3H); 2.33 ppm (m, 1H); 4.37 ppm (d, $J = 7.5$ Hz, 1H); 4.84-5.26 ppm (m, 2H); 5.68-6.22 ppm (m, 1H); 6.97-7.43 ppm (m, 4H). MS: M^+ 180; base peak at m/e 133. Deuterium content: 98% D_2 , 2% D_1 .

Metalation of thioether 17 at -78° and methylation at -15° . The same procedure as for 17 at -78° was used. The MeI iodide was added at -15° , after 0.5 hr. The products ratios are indicated in Table 2.

Metalation of 17 in tetrahydrofuran and hexamethyl phosphoramide (8:2). For the experiment in a mixture of THF and hexamethyl phosphoramide (8:2), the metalation was carried out at the indicated temp, and alkylating agent added after 0.5 hr. The product ratios are indicated in Table 4.

Metalation of methylallylthioether and alkylation with (1,1- $^2\text{H}_2$) benzylbromide. The same procedure described for non deuterated benzyl bromide was used. By chromatography on silica gel with petrol ether/benzene 98:2, we isolated 10% of 24 E + Z (1/1) and 25% of 23.

For compound 23. $^1\text{H NMR}$: $\delta = 1.90$ ppm (s, 3H); 3.16 ppm (d, $J = 7$ Hz, 1H); 4.62-5.10 ppm (m, 2H); 5.30-5.92 ppm (m, 1H); 7.12 ppm (s, 5H). MS: M^+ 180; base peak at m/e 77. Deuterium content: 97% D_2 , 3% D_1 .

For compounds 24 E + Z. $^1\text{H NMR}$: $\delta = 2.11$ ppm and 2.15 ppm (2s, 3H, 24 E and 24 Z SCH₃ groups respectively); 2.25 ppm (d, broad, $J = 7$ Hz, 2H); 5.05-6.10 ppm (m, 2H); 7.10 ppm (s, 5H). MS: M^+ 180; base peak at m/e 77. Deuterium content: 95% D_2 , 5% D_1 .

Synthesis of the allyl 1-(1,2,3,4-tetrahydro)-naphthyl thioether 25. 1-Bromo-1,2,3,4-tetrahydronaphthalene (prepared from α tetralone by reduction with LAH in ether followed by reaction with PBr_3 in benzene) (16.9 g) was added at 0° , to a soln of sodium alkylthiolate (prepared from allylmercaptan (5.7 ml) and NaOMe (1.1 eq) in MeOH (250 ml)). After 12 hr stirring at 20° , 25 was extracted and distilled under reduced pressure. The yield was 75%. B.p.: $98-102^\circ$ (0.05 mmHg). Colorless oil.

$^1\text{H NMR}$: $\delta = 1.55-2.50$ ppm (m, 4H); 2.55-2.95 ppm (m, 2H); 3.10 ppm (d, $J = 7$ Hz, 2H); 3.95 ppm (m, 1H); 4.90-5.30 ppm

(m, 2H); 5.52–6.10 ppm (m, 1H); 6.85–7.35 ppm (m, 4H). MS: M^+ 204; base peak at *m/e* 131 (Found: C, 76.6; H, 8.1. Calc. for $C_{13}H_{16}S_1$: C, 76.41; H, 7.90).

Metalation of allyl 1-(1,2,3,4-tetrahydro)-naphthyl thioether 25 and methylation at -78° . To a soln of **25** (0.61 g) and tetramethylethylenediamine (0.45 ml) in THF (30 ml), at -78° , BuLi (1 eq) was added. The medium turned orange. After 0.5 hr, MeI was added. The usual extraction with ether was utilised, yielding, after evaporation of the solvent, a colorless oil (0.67 g). The mixture was separated by chromatography on silica gel with petrol ether/benzene 98:2.

For compound 26 92% (Major/Minor: 2.5/1). 1H NMR: the two stereoisomers were separated by chromatography on silica gel. *Major*: δ = 1.28 ppm (d, J = 6.5 Hz, 3H); 1.55–2.25 ppm (m, 4H); 2.50–2.90 ppm (m, 2H); 3.32 ppm (q, J = 6.5 Hz, 1H); 3.92 ppm (m, 1H); 4.78–5.22 ppm (m, 2H); 5.33–6.10 ppm (m, 1H); 6.85–7.38 ppm (m, 4H). (Found: C, 76.9; H, 8.2. Calc. for $C_{14}H_{18}S_1$: C, 77.00; H, 8.31%). *Minor*: δ = 1.34 ppm (d, J = 6.5 Hz, 3H); 3.44 ppm (q, J = 6.5 Hz, 1H) all other peaks are identical to those of the major isomer. MS: M^+ 218; base peak at *m/e* 131.

For compound 27. 1H NMR: δ = 0.98 ppm (t, J = 7 Hz, 3H); 1.60–2.35 ppm (m, 6H); 2.55–2.92 ppm (m, 2H); 4.16 ppm (m, 1H); 5.42–6.10 ppm (m, 2H); 6.88–7.50 ppm (m, 4H). MS: M^+ 218; base peak at *m/e* 131.

Metalation of allyl 1-(1,2,3,4-tetrahydro)-naphthyl thioether 25 and methylation at -15° . To a soln of **25** (0.82 g) and tetramethylethylenediamine (0.7 ml) in THF (30 ml), at -15° , 1 eq of BuLi was added. After 0.5 hr at -15° , MeI was added. The usual extraction with ether was done yielding after evaporation of the solvent a yellowish oil (0.85 g). The mixture was separated by chromatography on silica gel with petrol ether.

35% of **28**; 35% of **29 E/Z** (3/1); 8% of **30 E**; **29 E + Z** and **30** were not separable by silica gel chromatography but by an additional gas chromatography separation on SE 30 30% Chromosorb W at 200° .

For compound 30. 1H NMR: δ = 1.64–1.98 ppm (m, 4H); 2.16 ppm (s, 3H); 2.54–2.90 ppm (m, 4H); 3.30 ppm (d, J = 6 Hz, 2H); 5.18–6.15 ppm (m, J = 15 Hz, 2H); 6.66–7.03 ppm (m, 3H). MS: M^+ 218; base peak at *m/e* 171 (Found: C, 77.0; H, 8.3. Calc. for $C_{14}H_{18}S_1$: C, 77.00; H, 8.31%).

Metalation of allyl 1-(1,2,3,4-tetrahydro)-naphthyl thioether 25 in tetrahydrofuran/hexamethyl phosphoramidate. For the experiment in THF/hexamethyl phosphoramidate (8:1), the metalation was carried out as for **25** in THF, at the indicated temp and alkylating agent added after 1 hr. Product ratio is indicated in Table 5.

Metalation of allyl 1-(1,2,3,4-tetrahydro)-naphthyl thioether 25 at -78° and methylation at -15° . The same procedure as for **18** at -78° was used except that the alkylating agent was added at -15° . Product ratio is indicated in Table 5.

Metalation of methyl allyl thioether and alkylation with 1-bromo-1,2,3,4-tetrahydronaphthalene. The metalation was done at -78° as previously described. After 0.5 hr, α -bromotetraline (1 eq) was added. Usual extraction with $CHCl_3$ yielded: 20% of **28** and 10% of **29 E/Z** (1:1).

For compound 28. 1H NMR: δ = 1.55–2.15 ppm (m); 1.85 and 1.92 ppm (2s), (7H); 2.50–3.60 ppm (m, 4H); 4.63–5.12 ppm

(m, 2H); 5.28–5.92 ppm (m, 1H); 6.76–7.20 ppm (m, 4H). MS: M^+ 218; base peak at *m/e* 131 (Found: C, 76.9; H, 8.0. Calc. for $C_{14}H_{18}S_1$: C, 77.00; H, 8.31%).

For compound 29 E/Z. 1H NMR: δ = 1.55–1.95 ppm (m, 4H); 2.15 and 2.19 ppm (2s, 3H, **29 Z** and **29 E** respectively); 2.25–3.00 ppm (m, 5H); 5.25–6.15 ppm (m, 2H); 6.88–7.20 ppm (m, 4H). MS: M^+ 218; base peak at *m/e* 131. (Found: C, 76.9; H, 8.5. Calc. for $C_{14}H_{18}S_1$: C, 77.00; H, 8.31%).

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REFERENCES

- J. E. Baldwin, J. de Bernardis and J. E. Patrick, *Tetrahedron Letters* 353 (1970); ^bU. Schöllkopf, K. Fellenberger and M. Ruk, *Liebigs Ann.* 734, 106 (1970); ^cU. Schöllkopf, *Angew. Chem.* 82, 795 (1970); *Ibid. Int. Ed. Engl.* 9, 763 (1970); ^dV. Rautenstrauch, *Chem. Commun.* 4 (1970); ^eJ. E. Baldwin and J. E. Patrick, *J. Am. Chem. Soc.* 93, 3556 (1971); ^fV. Rautenstrauch, *Helv. Chim. Acta* 54, 739 (1971).
- J. F. Biellmann and J. B. Ducep, *Tetrahedron Letters* 33 (1971).
- E. Vedejs and P. L. Fuchs, *J. Org. Chem.* 36, 366 (1971).
- T. Mukaiyama, S. Fukuyama and T. Kumamoto, *Tetrahedron Letters* 3787 (1968).
- ^aS. Tori, H. Tanaka and Y. Tomotaki, *Chem. Letters* 1541 (1974); ^bP. L. Stotter and R. E. Hornish, *J. Am. Chem. Soc.* 95, 4444 (1973); ^cJ. F. Biellmann and J. B. Ducep, *Organic Reactions* (1979) in press; ^dJ. B. Ducep, Thèse de Doctorat, Strasbourg (1971) No. AO 5292.
- J. F. Garst and C. D. Smith, *J. Am. Chem. Soc.* 95, 6870 (1973); J. F. Garst and C. D. Smith, *Ibid.* 98, 1520, 1526 (1976).
- R. Viau and T. Durst, *Ibid.* 95, 1346 (1973).
- E. L. Eliel, A. Abatjoglou and A. A. Hartmann, *Ibid.* 94, 4786 (1972).
- F. G. Bordwell *et al.*, *J. Org. Chem.* 42, 326 (1977).
- A. Streitwieser, Jr. and S. P. Ewing, *J. Am. Chem. Soc.* 97, 190 (1975).
- T. Laird and W. D. Ollis, *Chem. Commun.* 658 (1973).
- J. F. Biellmann and J. L. Schmitt, *Tetrahedron Letters* 4615 (1973).
- W. D. Ollis, R. Somathan and I. O. Sutherland, *Chem. Commun.* 661 (1973).
- H. Albrecht and J. Eichler, *Synthesis* 672 (1974); ^bJ. F. Garst, J. A. Pacifici, C. C. Felix and A. Nigam, *J. Am. Chem. Soc.* 100, 5974 (1978).
- K. H. Geiss, D. Seebach and B. Seuring, *Chem. Ber.* 110, 1833 (1977); K. H. Geiss, B. Seuring, R. Pieter and D. Seebach, *Angew. Chem.* 86, 484 (1974).
- H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.* 66, 1515 (1944).
- W. Ried, G. Deuschel and A. Kotelko, *Liebigs Ann.* 642, 121 (1961).