Tetrahedron. Vol. 32, pp 1801 to 1805. Pergamon Press 1976. Printed in Great Britain

REARRANGEMENT OF CARBANIONS AND OF YLIDES DERIVED FROM 4-THIACYCLOHEXENYL SYSTEMS

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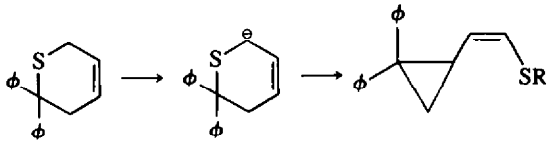
(*Received in UK* 19 *January* 1976; *Accepted for publication* 7 *March* 1976)

Abstract—The rearrangement of the carbanion and of the ylide derived from 5,5-diphenyl-4-thiacyclohexene to (E)2,2-diphenyl-1-methylthiovinylcyclopropane is shown to depend on the presence of a stabilizing substituent at C-5. A non concerted mechanism is proposed for this rearrangement. The carbanions from the 4-thiacyclohexene and from the sulfone of the 5,5-diphenyl-4-thiacyclohexene are stable. The cycloaddition of an aromatic thioketone to butadiene has been extended to an aliphatic thioketone.

In a previous communication,[1] we described the rearrangement of the carbanion **A** generated from the 5,5-diphenyl-4-thiacyclohexene **1** into a cyclopropyl thiolate **B** isolated as the methyl thioether **4**.

Now we report some further results of this rearrangement.



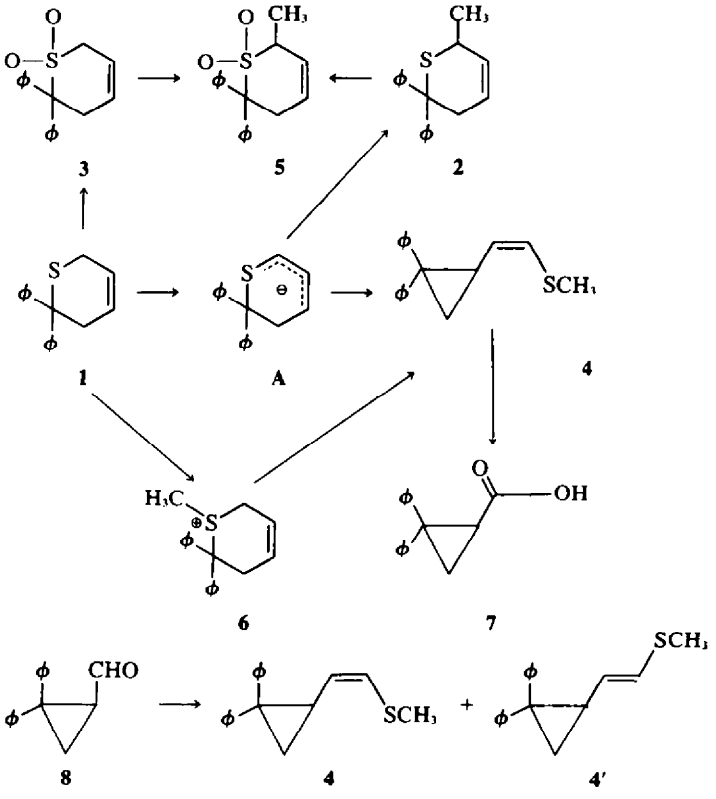
1 **A** **B**: R = ⊖ **4**: R = CH_3

Related carbanions derived from 4-thiacyclohexene have been used in the synthesis of the juvenile hormone of Cecropia.[2]

RESULTS

Preparation of starting materials. The 5,5-diphenyl-4-thiacyclohexene **1**, the 1,2-dimethyl-5,5-diphenyl-4-thiacyclohexene **9** and the 5-methyl-5-phenyl-4-thiacyclohexene **13** have been synthesised by a Diels–Alder reaction of aromatic thioketones and dienes.[3] In the same way we prepared the thioether **16** from adamantanethione[4] and butadiene.

In this case, the cycloaddition was more difficult. Whether this is due to the steric hindrance of the adamantane skeleton or to a slowing down of the reaction

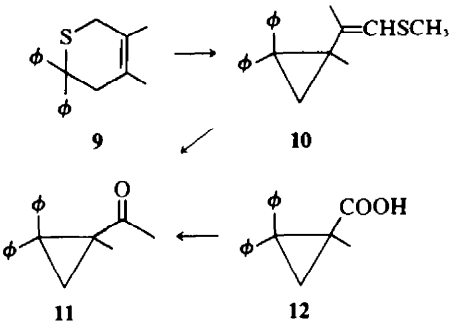


in the case of non conjugated thioketone, will not be discussed here. The cycloaddition of thioketone and other reactive C=S as thiophosgene to diene[5] needs mechanistic clarification. The thiacyclohexene-3 **22** has been prepared according to the literature.[6] The sulfones **3** and **17** and the sulfonium salts **6** and **20** have been prepared according to known procedures.[3,7,8]

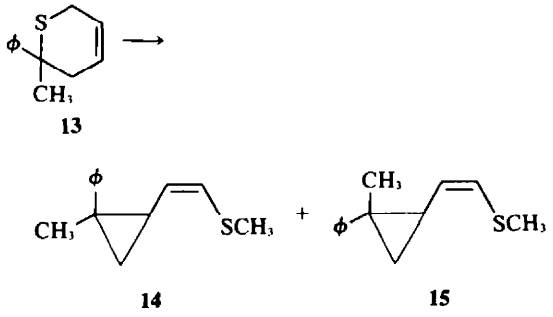
Reaction of **1** *with n-butyllithium.* At −78° in THF the thioether **1** was treated with n-BuLi in the presence of diazabicyclooctane (DABCO) or tetramethylethylene diamine (TMEDA). The alkylation by methyl iodide yielded the monomethylated product **2** which was converted into the sulfone **5**. The sulfone **5** was obtained from **3** by treatment with n-BuLi followed by methyl iodide. When the reaction was run at higher temperatures (from −40° to −15°) the *cis*-cyclopropane methyl thioether **4** was obtained. The product **4** was degraded into the 2,2-diphenylcyclopropane carboxylic acid **7**. The compound **4** was prepared from the 2,2-diphenylcyclopropane aldehyde **8** by a Wittig reaction using methyl mercapto methylenetriphenylphosphorane.[9] This last reaction also gave the *trans*-isomer **4'**. No trace of the *trans* product had been detected in the reaction of the rearrangement of the carbanion **A**.

In order to prove that the carbanion **A** rearranges into the thioenolate **B**, a solution of **A** was prepared at −78° (at this temp. the carbanion is stable). This solution was warmed up to −15° for 45 min, then cooled down again to −78° and methyl iodide added. The only isolated product was **4**.

Reactions of **9** *and* **13** *with* n-BuLi. The 1,2-dimethyl-5,5-diphenyl-4-thiacyclohexene **9** rearranged under the same reaction conditions. The resulting cyclopropyl-thioether **10** was transformed into (1-methyl 2,2-diphenyl)cyclopropyl methyl ketone **11** by ozonisation. The product **11** was found to be identical to the ketone obtained by reaction of methyllithium with (1-methyl 2,2-diphenyl)cyclopropane carboxylic acid **12**.



At −15° the carbanion derived from the thioether **13** rearranged into a 1:1 mixture of the cyclopropane vinyl thioethers **14** and **15** the structures of which were established by NMR.†



Reaction of **16** *with* t-BuLi. At −78° and 25° the thioether **16** gave the unrearranged α- and γ-methylated products **18** and **19**. The ratio α:γ was somewhat temperature dependent: 90:10 at −78° and −15° and 77:23 at 25°. At −15° and 25° a third product was isolated: its NMR spectrum did not correspond to the expected structure of the rearranged product.

†The shielding of the proton β to the sulfur by the phenyl group allows a tentative assignment to both isomers: for the first (δ = 4.58 ppm) structure **15** is suggested and the second (δ = 5.30 ppm) structure **14**.

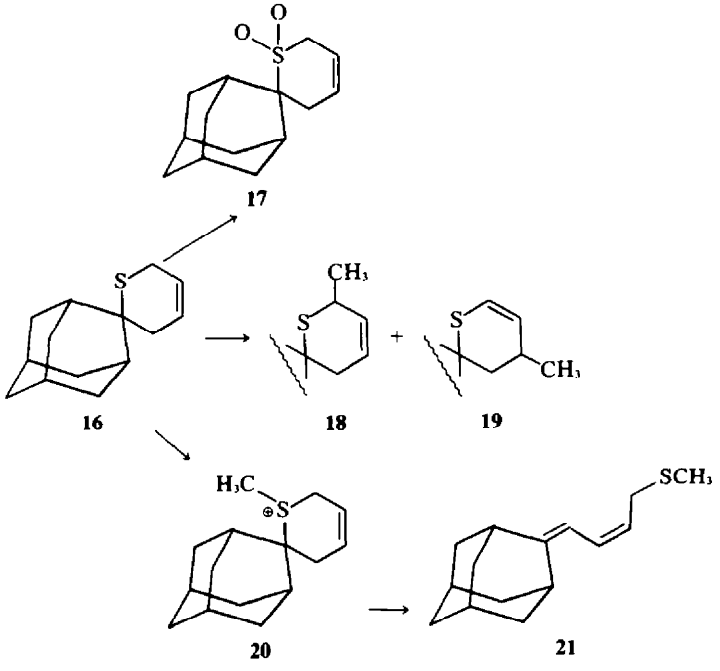
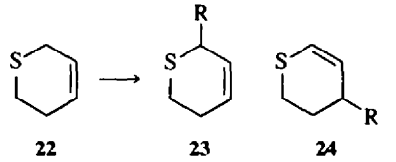


Table 1.

Essays	Solvant	t°C	t(H)	Substrate	α/γ*	Yield %
1	THF	−78°	1	$PhCH_2Br$	66/33	96
2	THF	−20°	24	CH_3I	66/33	90
3	THF	25°	6	CH_3I	66/33	60
4	THF/HMPT (30 ml:1 ml)	−11°	2	CH_3I	66/33	—

*Estimated from NMR spectrum.

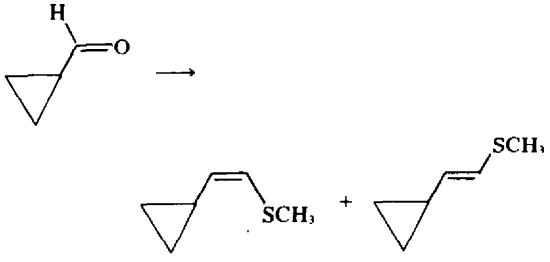
Reaction of **22** *with* t-BuLi. Under various reaction conditions (Table 1) C-alkylated products **23** and **24** were obtained.



22 **23** **24**

a: R = $CH_2\phi$
b: R = CH_3

The expected rearranged product **26** and its *trans*-isomer **26'** were prepared by a Wittig reaction.[9] None of the products **26** and **26'** were detected in the different reactions. In the runs 3 and 4 a third compound was obtained in a low yield. Experimental data showed that this product is different from **26** and **26'**.



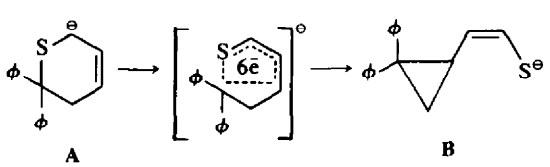
26 **26'**

Reactions of the ylides deriving from **6** *and* **20**. Rearrangements of sulfonium and ammonium ylides have been described.[10] At room temperature in THF the ylide generated from the methyl sulfonium **6** using potassium t-butoxide as a base yielded the cyclopropylvinyl thioether **4**. However the ylide from the sulfonium salt **20** using methanolic sodium hydroxyde as a base did not rearrange. The product **21** corresponding to an elimination was isolated in 70% yield.

DISCUSSION

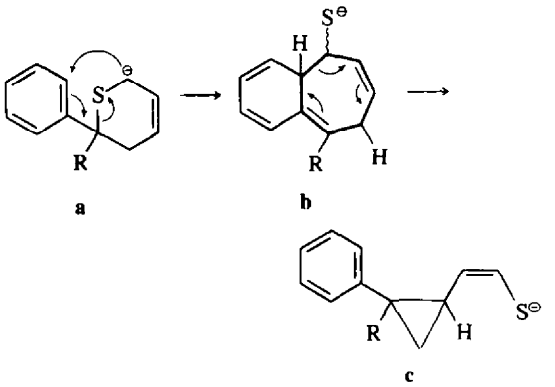
Three mechanisms for the rearrangement of 5-phenyl-substituted 4-thiacyclohexene to cyclopropylvinylthiolate may be proposed.[1]

(1) [1,4] Sigmatropic shift which may be concerted according to the Woodward–Hoffmann rules.[11]



A **B**

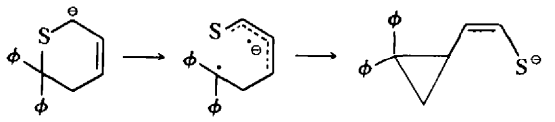
A [2,3] sigmatropic shift (Sommelet type rearrangement)[12] (**a**)→(**b**) followed by a [3,3] sigmatropic change of the cycloheptadiene to divinylcyclopropane (**b**)→(**c**) is excluded:



a **b** **c**

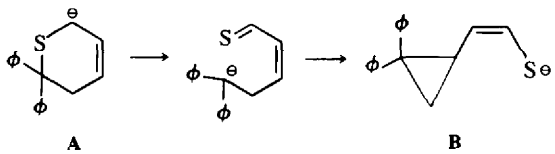
two shifts predict for **13** one epimer (**c**) and actually the two epimers are obtained.

(2) Homolytic fragmentation of the carbanion **A** to the radical anion and radical and recombination to **B**.[13]



A **B**

(3) Fragmentation to a carbanion and unsaturated thioaldehyde, and 1,4-addition of the carbanion to the unsaturated thioaldehyde.



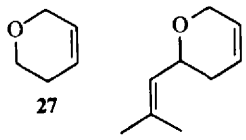
A **B**

Similar mechanisms apply to the rearrangement of the ylides.

In a first approximation, the phenyl group at the C-5 should have no effect in the case of the concerted [1,4] sigmatropic shift. The experiments described above apply to the carbanions as well as to the ylides, namely without a phenyl group at C-5, no rearrangement is observed. The two other mechanisms: homolytic or heterolytic fragmentation are preferred. The fact that only *cis*-cyclopropyl vinyl thioethers are obtained in the rearrangement, may reflect that the rotation around this bond is slow compared to the addition reaction (no data are available for the thioaldehyde and the radical anion derived from them). If

the radical mechanism proposed for the rearrangements of some carbanions and ylides proved to be general,[13] the homolytic cleavage may be preferred. Our present experimental data do not allow a choice.

It is interesting to discuss the different behaviour of the carbanions derived from 5-phenyl-4-thiacyclohexene and from 5,6-dihydro-2-pyrans **27** and **28**.[14a]



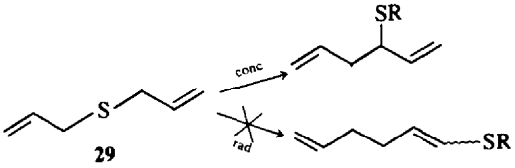
27

28

The carbanions from **27** and **28** rearrange into cyclopropyl enolates in conditions where the carbanion of 4-thiacyclohexene **22** does not rearrange even at higher temperature. It is to be noticed that the carbanion derived from **28** undergoes the rearrangement faster than the one from **27**. This is reminiscent of the necessity of a stabilising factor at the migrating center observed here.

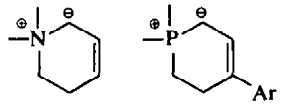
The different acidities of the compounds **22** and **27** may explain the difference in behaviour of the respective carbanions. Because the ether is less acidic than the thioether, the corresponding carbanion may have a higher energy. The activation energy for the rearrangement of dihydropyranne is then lowered. For the thiacyclohexenyl carbanion a stabilisation of the transition state is needed in order to observe the rearrangement.

An analogous difference in the reactivity of the carbanions derived from ether and thioether has been observed: in non-concerted mechanism conditions (hexane under reflux)[12] the treatment of diallyl sulfide **29** with n-BuLi always yields the product resulting from a concerted pathway; in the case of substituted diallyl ether the products araising from concerted and non-concerted mechanism are obtained.[14b,c,d]



29

For other types of ylides derived from ammonium **30**[15] and phosphonium **31**[16] salts of related structure, a similar rearrangement has not been detected.



30 **31**

In separate experiments, we prepared at low temperature the carbanion **A** which was converted into copper(I) derivative and lithium cuprate. The new species proved to be stable under conditions where the lithium compound rearranges. The copper compound could be alkylated by methyl iodide to **2** in a yield of 50% (not optimised) for the first and 100% for the cuprate. This agrees with a covalent bond between the carbon and the copper. The fact that the copper derivative does not rearrange as do certain lithium compounds, may be more general and may prove to be of synthetic value.

EXPERIMENTAL

Preparation of starting material. 5,5-diphenyl-4-thiacyclohexene **1**, 5-methyl-5-phenyl-4-thiacyclohexene **13**[3] and 4-thiacyclohexene **22** were prepared according to the lit.[6] 5,5-diphenyl-1,2-dimethyl-4-thiacyclohexene **9** was prepared in a manner similar to the product **1**. Compound **9** (yield 98%) was recrystallised from hexane: m.p.: 52–53°; NMR ($CDCl_3$): $\delta = 1.60$ (1 CH_3); $\delta = 1.75$ ppm (1 CH_3); $\delta = 2.70$–2.86 ppm (m, 4H); $\delta = 7.24$ ppm (m, H arom.). (Found: C, 81.6; H, 7.2. Calc. for $C_{19}H_{20}S$: C, 81.4; H, 7.2%).

Spiro (adamantane-2,2'-4-thiacyclohexene) **16**. A soln of thioadamantanone[4] (1.38 g) in butadiene (50 ml) was heated in a sealed tube at 100° for 24 hr. After evaporation of the excess butadiene, the residue was chromatographed on silicagel. The product (1.18 g) was obtained in the fraction hexane to hexane–benzene 9:1 and recrystallised from MeOH, m.p. 44–48°; NMR ($CDCl_3$): $\delta = 1.8$ ppm (m, 12H); $\delta = 2.56$ ppm (m, 4H); $\delta = 3.08$ ppm (m, 2H); $\delta = 5.57$ ppm (m, 2H). MS: M^+ at 220; m/e^+ at 166 (retro Diels–Alder).

Preparation of the sulfones **3** *and* **17**. The sulfone **3** derived from **1** was prepared according to the lit.[3] and the sulfone **17** was prepared from **16** by the same procedure. For the sulfone **17**: m.p.: 97–99° (from EtOH); NMR ($CDCl_3$): $\delta = 1.80$ ppm (m, 12H); $\delta = 2.88$ ppm (m, 4H); $\delta = 3.62$ ppm (m, 2H); $\delta = 5.66$ ppm (m, 2H). (Found: C, 66.9; H, 8.2. Calc. for $C_{14}H_{20}O_2S$: C, 66.7; H, 7.9%). MS: M^+ at 188 (loss of SO_2).

Preparation of the sulfonium **6** *and* **20**. These sulfoniums were prepared as fluorosulfonate salts from **1** and **16** by treatment with methyl fluorosulfonate according to the lit.[7]

For compound **6**: m.p. 200° (dec) from Et_2O; NMR (CD_3OD): $\delta = 1.62$ ppm (s, 3H); $\delta = 5.15$ ppm (m, 2H); $\delta = 7.02$ ppm (s, 10H); signals under MeOH signals. MS: $m/e^+ = 266$.

For compound **20**: m.p.: 98° (dec) from Et_2O; NMR ($CDCl_3$): $\delta = 1.98$ ppm (m, 12H); $\delta = 3.89$ ppm (m, 4H); $\delta = 1.72$ ppm (s, 3H); $\delta = 3.89$ ppm (s large, 2H); $\delta = 5.92$ ppm (m, 2H). MS: $m/e^+ = 235$.

Metalation of **1** *and methylation at* −78°

Preparation of **2**. A soln of **1** (1.2 g) and DABCO (0.50 g) in anhyd THF was cooled to −78°. A 1.1 equiv of n-BuLi soln was added slowly. After 1 hr, an excess MeI (0.3 ml) was added. After addition of water and ether, the ether layer was washed with water and dried over $NaSO_4$. After evaporation, the product **2** (95%) was recrystallised from hexane, m.p. 87.5–89.5°; NMR (CCl_4): $\delta =$ 1.20 ppm (1 CH_3) (J = 7 Hz); $\delta = 2.9$ ppm (m, 3H); $\delta = 5.9$–6.0 ppm (m, 1H); $\delta = 6.95$–7.53 ppm (m, 10H). MS: M^+ 266; m/e 198 (M^+-C_3H_8). (Found: C, 81.1; H, 6.7. Calc. for $C_{18}H_{18}S$: C, 81.4; H, 7.1%).

Oxidation to the sulfone **5**. This was prepared according to the lit.[3]; m.p.: 153–154° from EtOH. NMR ($CDCl_3$): $\delta = 1.35$ ppm (J = 7 Hz, 1 CH_3); $\delta = 3.23$ ppm (m, 1H); $\delta = 3.41$ ppm (m, 2H); $\delta = 5.33$ ppm (J = 10 Hz, d of m, 1H); $\delta = 5.96$ ppm (m, 1H); $\delta = 7.60$ ppm (H arom). (Found: C, 72.3; H, 6.2. Calc. for $C_{18}H_{18}O_2S$: C, 72.4; H, 6.1%). The same sulfone **5** was prepared at −15° from **3** (0.31 g) in THF (25 ml) by successive additions of BuLi (1 eq.) and MeI (1 eq.).

Metalation of **1** *and methylation at* −15°

Preparation of **4**. The metalation was done as above except that the temp was −15°. The product **4** was isolated in 95% yield, m.p. 61.5–62° from hexane; NMR (CCl_4): $\delta = 1.38$–1.65 ppm (m, 2H); $\delta = 2.15$ ppm (s, 1 CH_3); $\delta = 2.28$–2.68 ppm (m, 1H); $\delta = 4.71$ ppm (t, J = 9.5 Hz, 1H); $\delta = 5.74$ ppm (d, J = 9.5 Hz, 1H); $\delta = 7.15$ ppm (m, 10H); MS: M^+ 266. (Found: C, 81.3; H, 7.0. Calc. for $C_{18}H_{18}S$: C, 81.4; H, 7.1%). The same product **4** was obtained by metalation of **1** at −78°, heating to −15° and reaction with MeI at −15° or at −78° after cooling.

Preparation of **4** *from sulfonium* **6**. To a suspension of the fluorosulfonate of **6** (0.22 g) in THF (25 ml), t-BuOK (0.1 g) was added. After 48 hr stirring, the product was extracted with ether. After recrystallisation from cyclohexane, a product which was identical to **4** prepared above, was obtained in a yield of 90%.

Ozonisation of **4**. A soln of **4** (0.85 g) in methanol:methylene chloride (3:1; 15 ml), was heated at −30° with O_3. The ozonide was destroyed by H_2O_2 30% (15 ml) in the presence of NaOH (2 g). The product was oxidised with alkaline Ag_2O[17] and the acid was identified as **7**[18] by the usual criteria.

Synthesis of thioethers **4** *and* **4'**. To a soln of triphenylmethyl mercapto methylene phosphorane (2 mol) in THF (25 mg) prepared according to the lit,[9] **8** (0.42 g) was added. After 12 hr heating under reflux, the ppt was filtrated off and washed with ether. The solvents were removed. After chromatography on silica gel with hexane, a mixture of *cis* and *trans* isomers (0.33 g) was isolated. After two recrystallisations from hexane the pure *cis* isomer **4** was obtained: identical to that obtained from **1**.

The *trans*-isomer **4'** could not be completely freed from the *cis*-isomer. NMR (CCl_4): δ = 1.20–1.50 ppm (m); δ = 1.95 ppm (s); δ = 2.10–2.35 ppm (m); δ = 4.56 ppm (q, J = 15 Hz, 9H); δ = 6.03 ppm (d, J = 15 Hz); δ = 7.10 ppm (m).

Preparation of thioether **10** *from* **9**. Compound **10** was prepared at −15° from **9** by metalation with BuLi and methylation as described above for **1**. The yield was 98%, m.p. 70–71° from hexane; NMR (CCl_4): δ = 1.06 ppm (s, 3H); δ = 1.23 ppm (d, J = 5.5 Hz, 1H); δ = 1.41 ppm (d, J = 1.5 Hz, 3H); δ = 2.06 ppm (d, J = 5.5 Hz, 1H); δ = 2.11 (s, 3H); δ = 5.51 ppm (m, 1H); δ = 6.91–7.51 ppm (m, H arom.); MS: M^+ 294 (Found: C, 81.4; H, 7.6. Calc. for $C_{20}H_{22}S$: C, 81.6; H, 7.5%).

Ozonisation of thioether **10**. After treatment of **10** (0.95 g) at −30° in methanol:methylene chloride 1:3 (20 ml) with O_3, the ozonide was destroyed by Zn powder (0.4 g) and AcOH (2.5 ml). After ether extraction, the product **11** was recrystallised from MeOH, m.p. 83.5–85°; NMR ($CDCl_3$): δ = 1.21 ppm (s, 3H); δ = 1.45 ppm (d, J = 5 Hz, 1H); δ = 1.94 ppm (s, 3H); δ = 2.36 ppm (d, J = 5.5 Hz, 1H); J = 7.21 ppm (m, H arom.). This product was identical with **11** prepared from **12**[19] by action of MeLi.

Preparation of **14** *and* **15** *from* **13**. The same procedure as for **1** at −15° was used here. The two epimers were isolated in a yield of 97%. They were separated by gas chromatography on XE 60 20% on Chromosorb W45/60 mesh at 150°.

For compound **14**: NMR (CCl_4): δ = 0.7 ppm (q, J = 4 Hz; 5.5 Hz; 2H); δ = 1.35 ppm (s, 3H); δ = 1.65–2.06 ppm (m, 1H); δ = 2.26 ppm (s, 3H); δ = 5.3 ppm (q, J = 8 Hz; 9.5 Hz; 1H); δ = 7.16 ppm (m, 5H).

For compound **15**. NMR (CCl_4): δ = 0.91–1.2 ppm (m, 2H); δ = 1.41 ppm (s, 3H); δ = 1.56–2.01 ppm (m, 1H); δ = 2.21 ppm (s, 3H); δ = 4.53 ppm (t, J = 9.5 Hz, 1H); δ = 7.11 ppm (m, 5H).

Metalation of **16**. The same procedure as for **1** at −78°, at −15° and metalation at −75° except that t-BuLi was used followed by warming to 25° which gave a mixture of **18** and **19** in a yield 95% and 90%; for the experiment at 25°, 10% of an unknown product was detected. The ratio **18**:**19** was 9 at −78° and −15° and 3.5 at 25°. **18** and **19** were separated by chromatography on silica gel.

For compound **18**. NMR ($CDCl_3$): δ = 1.26 ppm (d, J = 7 Hz, 3H); δ = 1.70 ppm (10H); δ = 2.31–2.46 ppm (m, 2H); δ = 2.46–2.73 ppm (m, 2H); δ = 2.83–3.60 ppm (m, 1H); δ = 5.64 ppm (m, 2H). MS: M⁺ 234; *m/e* 166 (retro Diels–Alder). (Found: C, 77.0; H, 9.5. Calc. for $C_{15}H_{22}S$: C, 76.9; H, 9.4%).

For compound **19**. NMR ($CDCl_3$): δ = 1.07 ppm (d, J = 7 Hz, 3H); δ = 5.5 ppm (q, J = 7 Hz, 2 Hz; 1H). MS: M^+ 234 (Found: C, 76.9; H, 9.5%).

Preparation of **21**. A soln of the fluorosulfonate of **20** (0.24 g) in MeOH (20 ml) was treated with 2N NaOH in MeOH (30 ml). After 30 min at 20°, the product was extracted and proved to be homogeneous by all criteria. NMR ($CDCl_3$): δ = 1.80 ppm (12H); δ = 2.05 ppm (s, 3H); δ = 2.38 ppm (1H); δ = 2.97 ppm (1H); δ = 3.21 ppm (d, J = 8 Hz, 2H); δ = 5.27 ppm (d of t, J = 8 Hz; 10 Hz; 1H). MS: M^+ 234.

Metalation of **22**. The same procedure as for **1** at −78° except using t-BuLi was used. For the experiment at different temps, the metalation of **22** was carried out at −78° and the soln was warmed to the indicated temp. and the alkylating agent added after time t. The results are summarised in the Table 1.

For compound **23a**. NMR ($CDCl_3$): δ = 2.29 ppm (m, 2H); δ = 2.68 ppm (t, J = 5.5 Hz, 2H); δ = 2.92 ppm (d, J = 7.5 Hz, 2H); δ = 3.50 ppm (m, 1H); δ = 5.76 ppm (2H); δ = 7.21 ppm (5H). MS: M^+ 190, base peak at *m/e* 99. (Found: C, 75.69; H, 7.33. Calc. for $C_{12}H_{14}S$: C, 75.78; H, 7.36%).

For compound **24a**. NMR ($CDCl_3$): δ = 1.62–2.15 ppm (m, 2H); δ = 2.38–2.98 ppm (m, 5H); δ = 5.63 ppm (q, J = 18 Hz, 5.5 Hz; 1H); δ = 6.09 ppm (d, J = 18 Hz, 1H); δ = 7.26 ppm (5H). MS: M^+ 190; base peak at *m/e* 99. (Found C, 77.09; H, 7.30%).

Synthesis of **26** *and* **26'**. To a soln of phenylmethyl mercapto methylenephosphorane (5 mmol) in THF (50 ml) prepared according to the lit,[9] **25** (0.3 g) was added. After 12 hr heating under reflux, the ppt was filtrated off and washed with ether. The solvents were removed and the residue distilled. The products and residual THF were separated by preparative gas chromatography (OV 17% column at 80°): the *cis*-preceeds the *trans*-compound.

For compound **26**. NMR ($CDCl_3$): δ = 0.2–1.8 ppm (5H); δ = 2.28 ppm (s, 3H); δ = 5.0 ppm (t, J = 9.5 Hz, 1H); δ = 5.82 ppm (d, J = 9.5 Hz, 1H). MS: M^+ 114; *m/e*⁺ at 99.

For compound **26'**. NMR ($CDCl_3$): δ = 0.25–1.70 ppm (5H); δ = 2.21 ppm (s, 3H); δ = 5.08 ppm (q, J = 9 Hz, 15 Hz; 1H); δ = 6.04 ppm (d, J = 15 Hz, 1H). MS: M^+ 114; *m/e* 67.

Reaction of **A** *with cuprousiodide*

Methylation of the organocopper compound at −15°. A THF soln of **A** at −78° was prepared as described. After 1 hr, 1 equiv of cuprous iodide was added slowly. The soln became dark. After 1 hr, the temp was brought up to −15°. MeI was added after 45 min. After the usual workup the unrearranged product **2** (50%) was isolated and no rearranged compound **4** was detected.

Methylation of lithium cuprate derived from **A** *at* −15°. The lithium cuprate was prepared at −78° by addition of 0.5 eq of cuprous iodide to a soln of **A** in THF prepared as described. The reaction was run as for the cuprous compound. After addition of MeI, the unrearranged product **2** was obtained in a yield of 100%.

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