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THIOPHILIC REACTION OF t-BUTYLLITHIUM ON CYCLIC THIOETHERS

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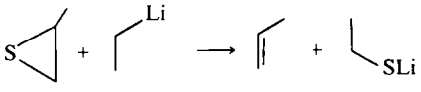
Abstract—The attack of t-butyllithium on the S atom of cyclic thioethers as 2,2-diphenyl thiacyclohexane and bicyclic analogues is described. The structure of the products are proved by physical data and synthesis. The driving factor for this reaction seems to be the stability of the carbanion formed.

Few thiophilic substitution reactions by carbanionic nucleophiles are known. Among them are the reactions of organometallic compounds with thioketones and dithioesters, in which addition of the organic moiety occurs at sulfur.[1-5] Most likely this reaction proceeds by an electron transfer mechanism, at least for thiobenzophenone, where the alkylthiodiphenylmethyl radical is observed.[6]

In the case of thioethers the attack of organolithium compounds on the S atom are known mainly for small thio rings: thiacyclopropane and thiacyclobutane.[7-9] For instance episulphide of propene reacts with ethyllithium by giving propene and lithiumethylthiolate:[8]



Other examples of thiophilic attack by carbanions have been described for the ring-opening of N-ethylisothiazole-3[10] and of 1,4-dithiacyclo 2,5-hexadiene[13] and for the racemization of optically active alkylaryl sulfoxides by alkyllithium.[11] This last reaction which proceeds with inversion at the S atom is proposed to go through a sulfurane like transition state. The reaction of vinyllithium on triphenylsulfonium fluoroborate is also supposed to occur by thiophilic substitution, leading here to a pentacoordinated sulfur intermediate.[12]

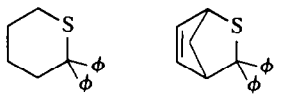
In the case of thiophilic attack on thioether, the driving force seemed to be the strain of the small ring, for no reaction had been observed for thiacyclopentane and thiacycloheptane.[8,9]

Looking at these results, we thought that other factors could interfere in the relative ease of thiophilic substitution: factors like the stabilisation of the expelled anion:

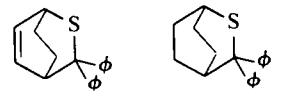
$$R_1-S-R_2+R_3Li \rightarrow R_1-S-R_3+R_2Li.$$

If the anion R_2^- stabilizes more easily the negative charge than anion R_3^-, and so has a lower basicity than R_3^-, the reaction will happen in the way described above.

Monocyclo- and bicyclo-thioethers disubstituted by phenyl groups at the α carbon to sulfur were prepared as follows: 2,2-diphenylthiacyclohexane **1** was obtained by hydrogenation of the corresponding thiacyclohexene; the addition of thiobenzophenone to 1,3-cyclopentadiene and 1,3-cyclohexadiene gave 3,3-diphenyl 2-thia(2:2:1) bicyclo 5-heptene **2** and 3,3-diphenyl 2-thia(2:2:2)-bicyclo 5-octane **3**; (respectively) from the latter 3,3-diphenyl 2-thia(2:2:2) bicyclooctane **4** was prepared by hydrogenation.

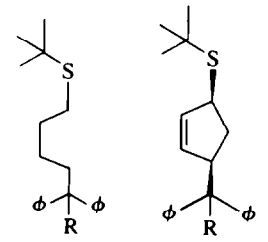


1 **2**

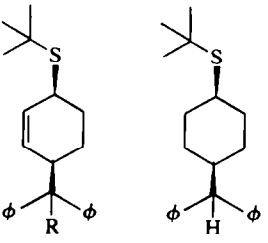


3 **4**

The t-butyllithium reacted with these compounds at 0° in THF in the presence of tetramethyl-ethylene-diamine (TMEDA). By addition of water or methyliodide to the red solutions, the t-butylthioethers **5**, **6** and **7** were obtained in high yield (80–100%). For the sulphide **4**, addition of hexamethylphosphortriamide was needed in order to obtain the thioether **8** in a 22% yield; 54% of starting material was recovered in this case.†



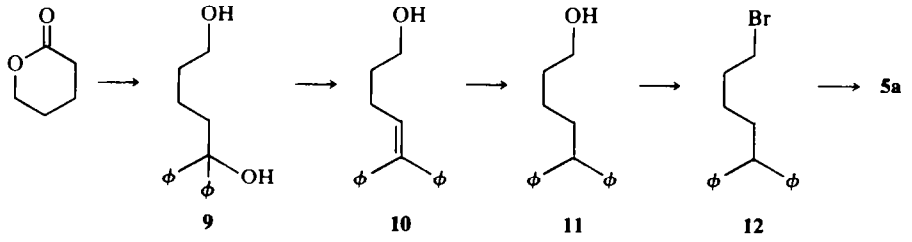
5a: R = H **6**: R = CH_3
b: R = CH_3



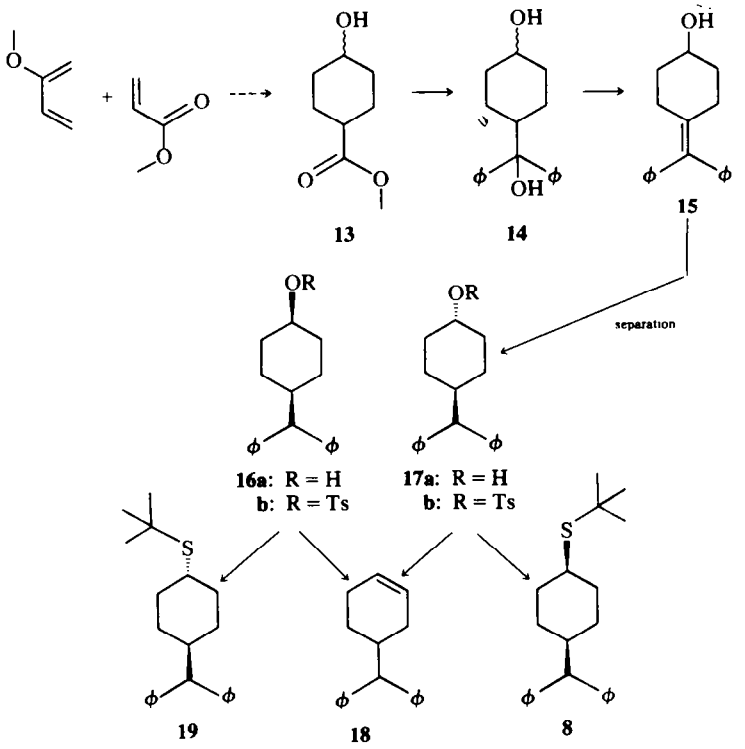
7a: R = H **8**
b: R = CH_3

†Part of t-butyllithium is destroyed by reaction with the medium: tetrahydrofurane or tetramethylethylenediamine.

The compound **5a** was synthesised according to Scheme 1:



The unsaturated thioether **7a** was reduced to the thioether **8** by hydrogenation in presence of Pd-C. The stereospecific synthesis of **8** was accomplished according to Scheme 2:



The earlier described hydrogenation of 4-hydroxybenzoic acid to the 4-carboxylic cyclohexanol[14] did not succeed in our hands. An alternative method starting from 2-methoxybutadiene and methylacrylate was used to obtain the desired starting material **13** as a mixture of epimers.[15] These were treated with phenylmagnesium bromide, followed by acid hydrolysis. The diols **14** were dehydrated to the alcohol **15**, which was reduced by hydrogen to a 5:3 mixture of the epimeric alcohols **16a** and **17a**. The two isomers were separated by chromatography and identified by NMR spectroscopy.

The signal attributed to the proton next to the OH group is 16 Hz broad for the isomer eluted first from the chromatography column, and is 30 Hz broad for the second one. In the two isomers the diphenylmethyl group, much larger than the OH group, is to be in an equatorial position. Consequently the first eluted product has the configuration **16a** and the second one corresponds to structure **17a**.

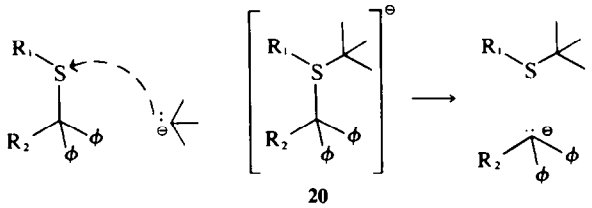
The tosylates **16b** and **17b** were prepared from the corresponding alcohols **16a** and **17a**.

The tosylate **17b** was refluxed in methanol in presence of sodium t-butylthiolate, giving the *cis*-thioether **8** in a 30% yield; starting material and an elimination product, diphenylmethyl-4 cyclohexene **18**, were recovered. Using the same reaction conditions for tosylate **16b**, the only product isolated was the elimination product **18**. However in hexamethyl-phosphortriamide at 120–140° in the presence of sodium t-butylthiolate tosylate **16a** gave 73% of diphenylmethyl-4 cyclohexene and 17% of the *trans*-thioether **19**.

The *cis*-thioether was identical to that obtained from the bicyclocompounds **3** and **4**.

The stereochemistry of the reaction products is in good agreement with a substitution mechanism: attack of the t-butyl anion at the S atom. In the ring-opening of these thioethers, the strain in the cycle is certainly not the main factor as it is to be supposed for thiacyclopropane and thiacyclobutane, but the lower basicity of the carbanion leaving the sulfur is here the driving force.†

†The lower reactivity of thioether **4** compared to the thioether **3** could be due to steric hindrance during the formation of **20**, or to the greater ring strain in **3** than in **4**: a strain energy difference of 4.3 kcal/mole is found for bicyclo (2.2.2)octane compared to bicyclo(2.2.2)octene.[17]

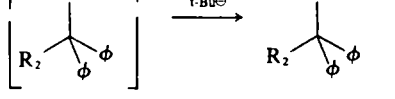


20

The first step of the thiophilic attack may be the occupation of the vaccant d orbitals of sulfur by the electron pair of the nucleophile.

Whether **20** is an intermediate or a transition state will not be discussed here. Recently an analogous substitution reaction by butyl-lithium was observed at the phosphorous atom of alkylarylphosphines; it is favoured in tetrahydrofurane compared to less polar solvants.[16]

Some authors have proposed a catalysis by the lithium cation.[7,8] However the attack on thioether **4** occurred only in the presence of hexamethylphosphortriamide, which is a good solvating agent for cations. This seems to exclude a mechanism involving fixation of the lithium cation by sulfur electron pairs, as described by the following scheme:



EXPERIMENTAL

Preparation of 2,2-diphényl thiacyclohexane **1**. This was prepared by hydrogenation of 2,2-diphenyl thiacyclohexene-4[18] (500 mg) in EtOH-EtOAC 1:1 (50 ml) in presence of 200 mg 10% Pd-C. The product was recrystallised from hexane, m.p.: 52–54°, yield 90%. H^1 NMR Spectrum ($CDCl_3$): 4 H m δ = 1.44–2.00 ppm; 4 H m δ = 2.51–2.94 ppm; 10 H m δ = 7.09–7.62 ppm. (Found: C, 80.11; H, 7.21. $C_{16}H_{18}S$: Calc.: C, 80.22; H, 7.09%).

Preparation of 3,3-diphenyl 2-thia(2.2.1)bicyclo heptene-5 **2**. Compound **2** was prepared according to Ref. 19 from cyclopentadiene and thiobenzophenone, (m.p.: 144–146°, m.p. lit.: 133–134°).

Preparation of 3,3-diphenyl 2-thia[2.2.2]bicyclooctane **3**. Compound **3** was prepared from cyclohexa-1,3-diene (15 ml) and thiobenzophenone (8 g). After five days under N_2 and in the dark, excess cyclohexadiene was removed. The product was recrystallised from benzene, m.p.: 210°, yield 89%. ^{1}H NMR Spectrum ($CDCl_3$): 4 H m δ = 1.15 to 2.2 ppm; 2 H large peak δ = 3.66 ppm; 1 H t δ = 6.25 ppm J_{HH} = 7.5 Hz; 1 H t δ = 6.48 ppm J_{HH} = 7.5 Hz; 10 H m δ = 6.98–7.66 ppm. (Found: C, 82.30; H, 6.60 $C_{19}H_{18}S$ Calc.: C, 81.98; H, 6.52%).

Preparation of 3,3-diphenyl 2-thio[2.2.2]bicyclooctane **4**. Compound **4** was prepared by hydrogenation of **3** (600 mg) in benzene (100 ml) in presence of 400 mg 10% Pd-C. The product **4** was recrystallised from benzene-hexane, m.p.: 185–185.5°, yield 100%. ^{1}H NMR Spectrum ($CDCl_3$): 8 H large peak δ = 1.77 ppm; 2 H large peak δ = 2.20 ppm; 10 H m δ = 7.00–7.70 ppm. (Found: C, 81.50; H, 7.18 $C_{17}H_{20}S$ Calc.: C, 81.38; H, 7.19%).

Reactions of t-butyllithium with thioethers

Reaction of t-butyllithium and 2,2-diphenyl thiacyclohexane **1**. To a soln of **1** (220 mg) and tetramethyl ethylene diamine (500 mg) in THF (20 ml) at −10° a soln of t-BuLi in pentane 12.8% (0.8 ml; 1.3 eq.) was added. The reaction medium turned deep red. After 1 hr, water or MeI was added. The usual extraction with ether was applied, yielding 100% **5a** as an oil. ^{1}H NMR Spectrum ($CDCl_3$): 9 H s δ = 1.28 ppm; 6 H m δ = 1.30–2.30 ppm; 2 H t δ = 2.45 ppm J_{HH} = 7 Hz; 1 H t δ = 3.87 ppm ∂_{HH} = 7.5 Hz; 10 H s δ = 7.22 ppm. (Found: C, 80.75; H, 9.18. $C_{20}H_{27}S$ Calc.: C, 80.76; H, 9.97%).

The methylated product **5b** was an oil (yield 90%) ^{1}H NMR Spectrum ($CDCl_3$): 9 H s δ = 1.27 ppm; 3 H s δ = 1.68 ppm; 8 H m δ = 1.31–2.92 ppm; 10 H s δ = 7.18 ppm. (Found: C, 79.37; H, 9.01. $C_{21}H_{29}S$ Calc.: C, 81.05; H, 8.67%).

Reaction of t-butyllithium and 3,3-diphenyl 2-thia(2.2.1)bicycloheptene-5 **2**. The same procedure as for **1** was used. MeI was added. Product **6** was recrystallised from hexane, m.p.: 121–123°, yield 96%. ^{1}H NMR Spectrum (CCl_4): 9 H s δ = 1.30–2.10 ppm; 1 H m δ = 2.60–3.10 ppm; 1 H m δ = 3.20–m δ = 2.3–2.63 ppm; 2 H m δ = 3.30 ppm; 10 H s δ = 7.09 ppm. (Found: C, 82.10; H, 8.40. $C_{23}H_{28}S$ Calc.: C, 82.08; H, 8.39%).

Reaction of t-butyllithium and 3,3-diphenyl 2-thia[2.2.2]bicyclooctene-5 **3**. Same procedure as for **1** was used. Water or MeI was added.

Product **7a** was recrystallised from hexane, m.p.: 81–82°, yield 80%. ^{1}H NMR Spectrum ($CDCl_3$): 9 H s δ = 1.31 ppm; 4 H m δ = 1.30–2.10 ppm; 1 H m δ = 2.60–3.10 ppm; 1 H m δ = δ = 3.20–3.40 ppm; 1 H d δ = 3.58 ppm J_{HH} = 11.5 Hz; 2 H m δ = 5.30–5.80 ppm; 10 H m δ = 7.00–7.40 ppm. (Found: C, 82.05; H, 8.50. $C_{23}H_{28}S$ Calc.: C, 82.08; H, 8.39%).

Product **7b** was recrystallised from hexane, m.p.: 86–88°, yield 80%. ^{1}H NMR Spectrum ($CDCl_3$): 9 H s δ = 1.31 ppm; 3 H s δ = 1.63 ppm; 4 H m δ = 0.90–2.20 ppm; 2 H m δ = 2.95–3.45 ppm; 2 H m δ = 5.72 ppm; 10 H m δ = 7.05–7.40 ppm. (Found: C, 82.40; H, 8.80. $C_{29}H_{30}S$ Calc.: C, 82.22; H, 8.63%).

Reaction of t-butyllithium and 3,3-diphenyl 2-thia[2.2.2]bicyclooctane **4**. To a soln of **4** (140 mg) and tetraméthylethylene diamine (0.40 ml) in THF (40 ml) and HMPT (2 ml) at 0°, t-BuLi in pentane 12.8% (3 eq) was added. After 2 hr at 0°, water was added. The products were separated by chromatography on 30 g silicagel (eluted with hexane-benzene). 80 mg of starting material **4** was recovered and 40 mg of **8** isolated (see below).

Hydrogenation of **7a**. **7a** (200 mg) in EtOH–EtOAc 1:1 (50 ml) was hydrogenated in presence of 200 mg of 10% Pd-C. The usual work up was applied. Product **8** was recrystallised from MeOH, m.p.: 100°, yield 81%. ^{1}H NMR Spectrum ($CDCl_3$): 9 H s δ = 1.30 ppm; 8 H m δ = 1.30–1.93 ppm; 1 H m δ = 1.90–2.35 ppm; 1 H m δ = 3.00 ppm; 1 H d δ = 3.60 ppm J_{HH} = 11 Hz; 10 H m δ = 7.05–7.35 ppm. (Found: C, 81.10; H, 9.00. $C_{23}H_{30}S$ Calc.: C, 81.59; H, 8.93%).

Synthesis of **5a**

Preparation of 5,5-diphenyl-1-hydroxy-pentene-4 **10**. The reaction of PhMgBr (prepared from Mg (1 g) and bromobenzene (5 g) in ether (15 ml)) with δ-valerolactone (1 g) in ether (10 ml) gave after chromatography on silicagel (eluted with hexane-EtOAc 1:1) **9** (20) characterised by its ^{1}H NMR spectrum ($CDCl_3$).

^{1}H NMR Spectrum ($CDCl_3$): 6 H m δ = 0.76–1.84 ppm; 2 H t δ = 2.27 ppm J_{HH} = 7.5 Hz; 2 H m δ = 2.49–3.15 ppm; 2 H t δ = 3.48 ppm J_{HH} = 5.5 Hz; 10 H s δ = 7.27 ppm. The crude diol **9** (900 mg) in EtOH (30 ml) was treated with HCl (0.5 ml). After 30 min refluxing, the products were isolated by extraction with ether and separated by chromatography on silicagel. The expected **10** was eluted with hexane-EtOAc 4:1 as an oil;[18] yield 75%. ^{1}H NMR Spectrum ($CDCl_3$): 2 H m δ = 1.40–1.94 ppm; 3 H m δ = 1.94–2.40 ppm; 2 H t δ = 3.54 ppm J_{HH} = 6.5 Hz; 1 H t δ = 6.05 ppm J_{HH} = 7.5 Hz; 10 H s δ = 7.16 ppm.

Reduction of **10** *into 5,5-diphenyl-pentanol-1* **11**. The catalytic hydrogenation of **10** (100 mg, 0.4 mM) in EtOH–EtOAc 1:1 (2.5 ml) in presence of 20 mg 10% Pd-C afforded **11** as an oil,[22] yield 98%. ^{1}H NMR Spectrum ($CDCl_3$): 6 H m δ = 1.84–2.31 ppm; 2 H t δ = 3.53 ppm J_{HH} = 6.5 Hz; 1 H t δ = 3.87 ppm J_{HH} = 8 Hz; 1 H s δ = 4.27 ppm; 10 H s δ = 7.18 ppm; Mass spectrum M^+ = 240; base peak at *m/e* 167.

Preparation of 1-bromo-5,5-diphenyl-pentane **12**. Alcohol **11**

(80 mg) in ether (10 ml) was treated with PBr_3 (50 mg) in presence of a few drops HBr. After 10 days, water was added and the product extracted as usual. The product **12** was isolated as an oil,[23] yield 98%. ^{1}H NMR Spectrum ($CDCl_3$): 2 H m δ = 1.17–1.71 ppm; 4 H p δ = 2.00 ppm J_{HH} = 7.5 Hz; 2 H t δ = 3.34 ppm J_{HH} = 6.5 Hz; 1 H t δ = 3.87 ppm J_{HH} = 7.5 Hz; 10 H s δ = 7.20 ppm: Mass spectrum M^+ = 304; base peak at *m/e* 167.

Preparation of the thioether **5a**. Bromide **12** (100 mg) was added to a soln of a sodium t-butyl thiolate (large excess) in MeOH (20 ml). After an hr the product was extracted and identical to the product previously obtained by comparison of NMR and mass spectra and chromatographic behavior, yield 100%. (Found: C, 80.51; H, 9.07; $C_{20}H_{27}S$ Calc.: C, 80.76; H, 9.97%).

Synthesis of thioether **8a** *and its epimer* **19**

Preparation of alcohol **15**. The reaction (0.5 hr refluxing) of PhMgBr (prepared from Mg (400 mg) and bromobenzene in 50 ml of ether) with **13** (800 mg) gave a mixture of diols which were deshydrated by HCl (0.5 ml) in EtOH (30 ml). After 3 hr of reflux of products were isolated by the usual procedure and chromatography on 50 g silicagel column. Alcohol **15** (230 mg) was eluted with hexane-EtOAc 3:1 and recrystallised from hexane-MeOH, m.p. 153–154.5°. ^{1}H NMR Spectrum ($CDCl_3$): 9 H m δ = 1.30–1.80 ppm; 1 H sept. δ = 3.93 ppm J_{HH} = 8.5 Hz, J_{HH} = 4 Hz. 10 H m δ = 7.20 ppm; UV spectrum (EtOH) λ_{max} = 244 nm ϵ = IR spectrum ($CHCl_3$) 3600 cm^{-1} ν_{OH}; 1600 cm^{-1} $\nu_{C=C}$: (Found: C, 86.15; H, 7.59; $C_{17}H_{20}O$ Calc.: C, 86.32; H, 7.63%).

Preparation of alcohol **16a** *and* **17a**. The unsaturated alcohol **15a** (250 mg) in a soln of hexane-EtOAc 1:1 (30 ml) was hydrogenated in presence of 150 mg 10% Pd-C. After 4 hr the absorption was complete and the usual work up performed. The epimers were isolated by chromatography on 25 g silicagel (eluted with hexane-EtOAc 6:4). The *cis*-**16a** was eluted before the *trans*-**17a**.

Data for **16a**, m.p. 162.5–163° (hexane-EtOH). ^{1}H NMR Spectrum ($CDCl_3$): 9 H m δ = 1.10–1.00 ppm, 1 H m δ = 1.90–2.30 ppm. 1 H d δ = 3.65 ppm J_{HH} = 10.5 Hz; 1 H m δ = 3.97 ppm; 10 H s δ = 7.25 ppm: Mass spectrum M˙ 288; base peak at *m/e* 167. (Found: C, 85.73; H, 8.14. $C_{17}H_{22}O$ Calc.: C, 85.67; H, 8.32%).

Data for **17a**, m.p. 151–152.5° (hexane-EtOH). ^{1}H NMR Spectrum ($CDCl_3$): 10 H m δ = 0.70–2.30 ppm. 1 H d δ = 3.44 ppm J_{HH} = 10.5 Hz; 1 H m δ = 3.52 ppm; 10 H s δ = 7.25 ppm. Mass spectrum M˙ 266; base peak at *m/e* 167.

Preparation of the tosylates **16b** *and* **17b**. A soln of **16a** or **17a** (110 mg) in pyridine (2 ml) and tosylchloride (190 mg) was left at −6° for 3 days. The soln was poured on ice and the product extracted with ether.

Data for **16b**. ^{1}H NMR Spectrum: 9 H m δ = 0.70–2.30 ppm; 3 H s δ = 2.40 ppm; 1 H d δ = 3.46 ppm J_{HH} = 10.5 Hz; 1 H m δ = 4.75 ppm; 10 H s δ = 7.23 ppm; 2 H d δ = 7.36 ppm J_{HH} = 8 Hz; 2 H d δ = 7.80 ppm J_{HH} = 8 Hz.

Data for **17b**. ^{1}H NMR Spectrum ($CDCl_3$): 9 H m δ = 0.70–2.30 ppm; 3 H s δ = 2.40 ppm; 1 H d δ = 3.38 ppm J_{HH} = 10.5 Hz; 1 H m δ = 4.35 ppm; 10 H s δ = 7.18 ppm; 8 H d δ = 7.25 ppm J_{HH} = 8 Hz. 2 H d δ = 7.75 ppm J_{HH} = 8 Hz. Mass spectrum M^+ = 420; base peak at *m/e* 167.

Synthesis of thioether **8**. To a soln of NaOMe (1.3 mmol) in MeOH (4 ml) t-butylthiol (0.50 g) was added. The tosylate **17b** (30 mg) in MeOH (3 ml) was added and the soln refluxed for 12 hr. The products were separated by chromatography on 16 g silicagel. The derivative **18** (6 mg), the thioether **8** (7 mg) and the tosylate **17b** (10 mg) were eluted in this order with hexane-benzene.

Diphenylmethyl-4 cyclohexene **18**. ^{1}H NMR Spectrum ($CDCl_3$); 7 H d δ = 0.80–2.70 ppm, 3.57 ppm; 2 H m δ = 5.65 ppm J = 10.5 Hz; 10 H m δ = 7.23 ppm: Mass spectrum M˙ = 248; peak at *m/e* 167 and 152. The thioether **8** was identical to the product prepared by hydrogenation of **7a**, by comparison of NMR and mass spectra, chromatographic behavior and m.p.

Synthesis of thioether **19**: A soln of **16b** (41 mg) in HMPT (2 ml) in presence of sodium t-butylthiolate (1 mM) was heated at 120° for 12 hr. After the usual procedure, the products were separated by chromatography on silicagel (hexane-benzene), **18** (18 mg) and thioether **19** (6 mg).

Thioether **19**. ^{1}H NMR Spectrum ($CDCl_3$): 9 H s δ = 0.7–2.7 ppm, 1.30 ppm; 1 H d δ = 3.42 ppm J = 10 Hz; 10 H δ = 7.28 ppm. Mass spectrum M^+ = 388; peak at *m/e* 281, 247, 167 and 115.

REFERENCES

[1] M. Dagonneau and J. Vialle, *Bull. Soc. Chim. Fr.* 2067 (1972).
[2] P. Beak and J. W. Worley, *J. Am. Chem. Soc.* **92**, 4142 (1970).
[3] P. Metzner and J. Vialle, *Bull. Soc. Chim. Fr.* 1703 (1973).
[4] M. Dagonneau, D. Paquer and J. Vialle, *Ibid.* 1699 (1973).
[5] D. Paquer and J. Vialle, *C. R. Acad. Sci. Paris* **275**, 589 (1972).
[6] M. Dagonneau, J. F. Hemidy, D. Cornet and J. Vialle, *Tetrahedron Letters* 3003 (1972).
[7] D. C. Dittmer, P. L. F. Chang, F. A. Davis, I. K. Stamos and K. Takahashi, *J. Org. Chem.* **37**, 1116 (1972).
[8] F. G. Bordwell, H. M. Andersen and B. M. Pitt, *J. Am. Chem. Soc.* **76**, 1082 (1954).
[9] M. Morton and R. F. Kammereck, *Ibid.*, **92**, 3217 (1970).
[10] W. D. Crow and I. Gosney, *Tetrahedron* **26**, 3217 (1970).
[11] T. Durst, M. J. Lebelle, R. van den Elzen and K. C. Tin, *Can. J. Chem.* **52**, 761 (1974).
[12] B. M. Trost, R. Larocchelle and R. C. Atkins, *J. Am. Chem. Soc.* **91**, 2175 (1969).
[13] W. E. Parham and M. T. Kneller, *J. Org. Chem.* **23**, 1702 (1958).
[14] T. A. Giudici and T. C. Bruice, *Ibid.*, **35**, 2387 (1970).
[15] J. I. Degraw, *Ibid.*, **26**, 1156 (1961).
[16] E. P. Kyba and C. W. Hudson, *Tetrahedron Letters* 1869 (1975).
[17] N. L. Allinger and J. T. Sprague, *J. Am. Chem. Soc.* **94**, 5734 (1972).
[18] A. Ohno, Y. Ohnishi and G. Tsuchihashi, *Tetrahedron* **25**, 871 (1969).
[19] E. K. Yamada, M. Yoshioka and N. Sugiyama, *J. Org. Chem.* **33**, 1240 (1968).
[20] G. Wittig and O. Bob, *Liebigs Ann.* **566**, 113 (1950).
[21] G. Descotes and J. L. Soula, *Bull. Soc. Chim.* **10**, 2636 (1964).
[22] H. Gilman and B. T. Gas, *J. Org. Chem.* **28**, 1725 (1963).
[23] G. Benoit, R. Delavigne and F. Eliopoulo, *Ann. Pharm. Franç.* **10**, 181 (1952).