Novel chemical behaviour of a [2,3] sigmatropic rearrangement product of 2-phenyltetrahydrothiopyranium 1-methylide

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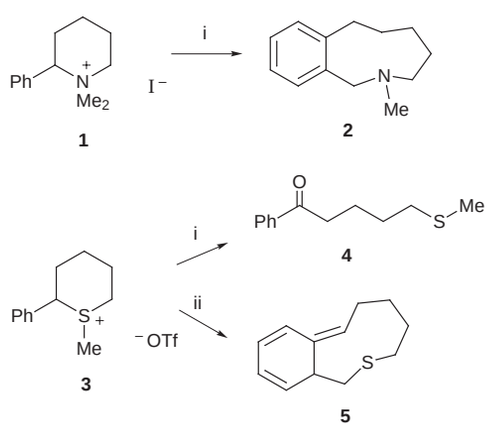
1,3,4,5,6,11a-Hexahydro-7*E*-2-benzothionine 5, which is a [2,3] sigmatropic rearrangement product of 2-phenyltetrahydrothiopyranium 1-methylide 8, has been synthesized by reaction of 1-methyl-2-phenyltetrahydrothiopyranium triflate 3 with sodium amide in liquid ammonia or by the fluoride ion-induced desilylation of *trans*-2-phenyl-1-[(trimethylsilyl)methyl]tetrahydrothiopyranium perchlorate *trans*-7. Compound 5 is stable at room temperature and reverts to ylide 8 by ring-opening.

Introduction

Sommelet–Hauser rearrangement of α-aryl-substituted cyclic ammonium and sulfonium alkylides is useful for synthesizing medium-sized heterocyclic compounds by three-carbon ring enlargement.[1] The reaction of 1,1-dimethyl-2-phenylpiperidinium iodide **1** with sodium amide in liquid ammonia gave 2-methyl-2,3,4,5,6,7-hexahydro-1*H*-2-benzazonine **2** (83%) by ylide rearrangement (Scheme 1).[2] However, similar treatment of



Scheme 1 *Reagents and conditions*: i, $NaNH_2$, liquid NH_3, 3 h, in air; ii, $NaNH_2$, liquid NH_3, 3 h, under N_2

1-methyl-2-phenyltetrahydrothiopyranium trifluoromethanesulfonate (triflate) **3** did not give the corresponding ring-enlargement product 1,3,4,5,6,7-hexahydro-2-benzothionine **12**, but rather gave 5-methylsulfanyl-1-phenylpentan-1-one **4** (57%).

The carbonyl oxygen of compound **4** should originate from air because the reagents and the solvent used do not have available oxygens. When the reaction was carried out under nitrogen, the product changed to 1,3,4,5,6,11a-hexahydro-7*E*-2-benzothionine **5** (isotoluene compound, 62%). These results led us to question whether products **4** and **5** were formed from the same intermediate. Fluoride ion-induced desilylation of [(trimethylsilyl)methyl]-ammonium and -sulfonium salts is an excellent method for regioselective ylide formation.[3,4] We report here the reaction of *trans*-2-phenyl-1-[(trimethylsilyl)methyl]-tetrahydrothiopyranium perchlorate **7** with caesium fluoride.

Results and discussion

Treatment of 2-phenyltetrahydrothiopyran **6** with (trimethylsilyl)methyl triflate followed by sodium perchlorate gave 2-phenyl-1-[(trimethylsilyl)methyl]tetrahydrothiopyranium perchlorate **7** as a single product, which was temporarily considered to have a *trans* configuration (Scheme 2).

The reaction of *trans*-**7** with caesium fluoride at 0 °C in DME under nitrogen gave a 75:21:4 mixture of products **5** ([2,3] sigmatropic rearrangement product of ylide **8**), **6** (demethylene product of **8**) and (*E*)-methylsulfanyl-1-phenylpent-1-ene **11** (Hoffmann degradation product of ylide **8**) in a total yield 54% after 3 h of stirring. However, the total yield decreased to 37% and the proportions changed to 55:29:14 when the same reaction was quenched after 24 h of stirring (Scheme 2, Table 1, entries 1 and 2). The yield of compound **11** increased when the reaction was carried out at 25 °C, and compound **11** became the main product at 70 °C (entries 3 and 4). Prolongation of the reaction time produced similar changes in the total yield and the product proportions in the reaction in DMSO, although appreciable amounts of compound **4** and 1,3,4,5,6,7-hexahydro-2-benzothionine **12** (Sommelet–Hauser rearrangement product) were formed (compare entries 9 and 10).

We previously reported that bicyclic isotoluene compounds, which are formed by [2,3] sigmatropic rearrangement of ylides in non-basic media, are mostly stable at rt and are aromatized to Sommelet–Hauser rearrangement products by the aid of a strong base, *e.g.* in the presence of DBU or in a solution of potassium hydroxide in ethanol.[4,5] When the reactions in entries 2, 3 and 10 were repeated in the presence of DBU, the yield of compound **12** increased at 25 °C with a decrease in that of compound **5**, whereas there was little change at 0 °C (compare entry 3 with 6, 10 with 11, and 2 with 5). These results show that compound **5** was fairly stable in basic media at lower temperature, and are consistent with the fact that compound **5** was not aromatized in a solution of sodium amide in liquid ammonia at −40 °C.

When the reaction in DME was carried out in air, the amount of acyclic ketone **4** did not increase in the presence of DBU, while the product became a complex mixture in the absence of DBU (entries 7 and 8). Thus in the reaction of compound *trans*-**7** with caesium fluoride, there was little formation of ketone **4** and air did not appear to have any effect; that is, compound **4** was not formed from ylide **8**.

Prolongation of the reaction time decreased the total yields and changed the product proportions; the yields of compounds **6** and **11** increased and that of the isotoluene **5** decreased (compare entry 1 with 2, and 9 with 10). When compound **5** was dissolved again in DME and the solution stirred at rt for 20 h, however, no appreciable changes were observed, while aromatization to compound **12** was completed after 72 h in the presence of DBU (Table 2, entries 1–3). In a DMSO solution, half of bicycle **5** was aromatized to compound **12** after 20 h in the absence of DBU (entry 4). Compounds **6** and **11** did not appear. On the other hand, when compound **5** was dissolved in

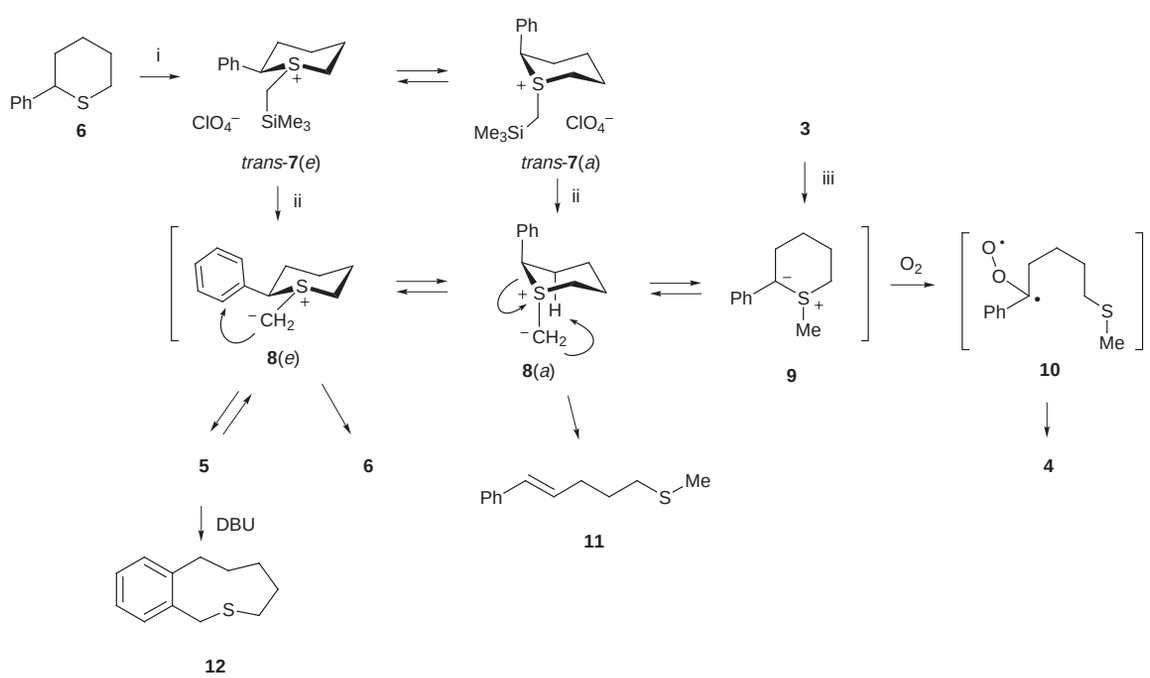
Table 1 Reaction of *trans*-2-phenyl-1-[(trimethylsilyl)methyl]tetrahydrothiopyranium perchlorate *trans*-**7** with CsF

	Reaction conditions						Product proportions[a]				
Entry	Solvent	Atmosphere	Additive	Temp. (*T*/°C)	Time (*t*/h)	Total yield (%)	**4**	**5**	**6**	**11**	**12**
1	DME	N_2		0	3	54	0	75	21	4	0
2	DME	N_2		0	24	37	2	55	29	14	0
3	DME	N_2		25	24	45	2	38	15	43	2
4	DME	N_2		70	24	85	0	0	<1	>98	<1
5	DME	N_2	DBU	0	24	41	6	59	13	13	9
6	DME	N_2	DBU	25	24	93	0	9	38	37	16
7	DME	Air		25	3			Complex mixture			
8	DME	Air	DBU	25	3	54	4	20	34	36	6
9	DMSO	N_2		25	3	67	0	67	0	28	5
10	DMSO	N_2		25	24	47	11	17	15	38	19
11	DMSO	N_2	DBU	25	24	77	1	0	24	25	50

[a] Proportions of the products were determined by integration of the ^1H signals at 400 MHz.

Table 2 Change in 1,3,4,5,6,11a-hexahydro-7*E*-2-benzothionine **5** at room temperature

					Product proportions			
Entry	Solvent	Base	Time (*t*/h)	Yield (%)	**5**	**6**	**11**	**12**
1	DME		20	85	100	0	0	0
2	DME	DBU	20	93	35	0	0	65
3	DME	DBU	72	96	0	0	0	100
4	DMSO		20	83	44	0	0	56
5	EtOH	10% KOH	20	77	0	30	51	19



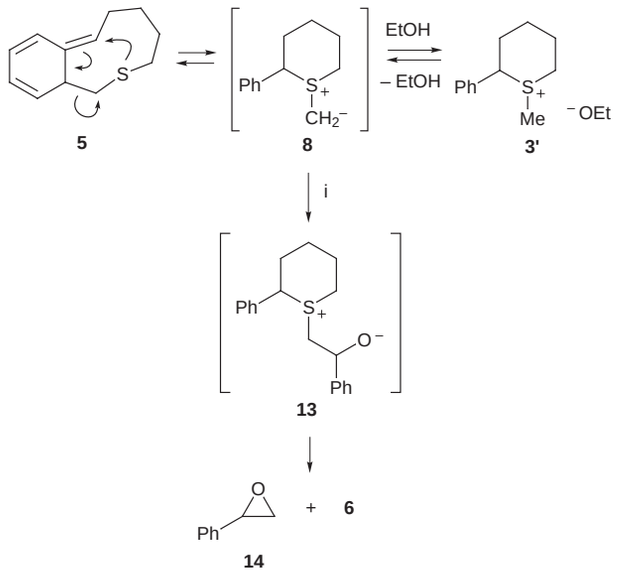
Scheme 2 *Reagents and conditions*: i, Me_3SiCH_2OTf, CH_2Cl_2, $NaClO_4$; ii, CsF, DME or DMSO, −40 °C, rt or 70 °C, 3–24 h; iii, $NaNH_2$, liquid NH_3, 3 h

a solution of 10% potassium hydroxide in ethanol and the solution kept for 20 h, compounds **6** and **11** were competitively formed with aromatization to compound **12** (entry 4).

It is unlikely that compounds **6** and **11** were formed directly from compound **5** because the former is a demethylene product of ylide **8** and the latter is a Hofmann degradation product. This result suggests that ylide **8** was present in the solution. A solution of compound **5** and benzaldehyde in DME in a ratio of 1 : 1, when stored at rt for 20 h, gave a mixture of substrate **5** (45% recovery), compound **6** (49%) and 2-phenyloxirane **14** (47%) (Scheme 3). Compounds **6** and **14** are the products of the reaction of ylide **8** with benzaldehyde.[6]

A reverse reaction of bicycle **5** to ylide **8** occurs in competition with aromatization to compound **12**, and may cause the above mentioned decrease in the total yields and the change in product proportions with prolongation of the reaction time. The equilibrium between compounds **5** and **8** lies to the right in an ethanol solution due to the contribution of sulfonium ethoxide **3′**, and thus gave mainly compounds **6** and **11** rather than compound **12** (Schemes 2 and 3). Although the equilibrium almost lies to the left in DME, since no change occurred when compound **5** was dissolved in DME, the reaction of ylide **8** with benzaldehyde resulted in high yields of products **6** and **14**.

Since the ratio of diaxial conformers **7**(*a*) and **8**(*a*) to diequatorial conformers **7**(*e*) and **8**(*e*) may increase with an increase in temperature, the yield of acyclic compound **11** which is generated from ylide **8**(*a*) increases at higher temperature (Scheme 2). Benzylide **9** is initially formed in the reaction



5 8 3' 13 14

Scheme 3 *Reagents and conditions*: i, PhCHO, DME, rt, 20 h

of compound **3** with sodium amide in liquid ammonia, and then comes into equilibrium with ylides **8**(*a*) and **8**(*e*).[7] In air, rapid oxidation of compound **9** with oxygen leads to ketone **4**, whereas isomerization to ylide **8** becomes the main path under nitrogen. The relative energy of isomer **8**(*e*) is 3.2 kcal mol^{-1}† lower than that of isomer **8**(*a*), and that for ylide **9** is 2.2 kcal mol^{-1} lower than that for ylide **8**(*e*) based on calculations at the Becke3LYP/6-31G* level.[8] These small differences in energy may allow the equilibrium among isomers **8**(*a*), **8**(*e*) and **9** to occur.

Experimental

DME, DMSO and DBU were dried by distillation from CaH_2. CsF was dried over P_2O_5 at 180 °C under reduced pressure. Distillation was performed on a Büchi Kugelrohr distillation apparatus. All mps (Yananco micro melting point apparatus) and bps (oven temperature) are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-A500, LA-400 or EX-270 spectrometer. *J*-Values are given in Hz. IR spectra were obtained on a Jasco FT-IR 5300 spectrometer, and UV-visible spectra were measured on a Shimadzu UV-240 spectrophotometer.

1-Methyl-2-phenyltetrahydrothiopyranium trifluoromethanesulfonate (triflate) 3

Methyl triflate (7.80 g, 47.5 mmol) was added to a solution of 2-phenyltetrahydrothiopyran[9] **6** (5.84 g, 32.7 mmol) in CH_2Cl_2 (50 cm^3) at rt and the mixture was stirred for 3 h. The solvent was evaporated off under reduced pressure and the residue was washed with Et_2O to give the *title salt* **3** (10.98 g, 95%), mp 81–82 °C (Found: C, 45.3; H, 5.0. $C_{13}H_{17}F_3O_3S_2$ requires C, 45.6; H, 5.0%); ν_{max}(KBr)/cm^{-1} 3023, 2934, 1424, 1262, 1163, 1030 and 639; δ_H(500 MHz; $CDCl_3$; Me_4Si) 1.89–2.19 (4 H, m), 2.39–2.46 (2 H, m), 2.82 (3 H, s), 3.78–3.90 (2 H, m), 4.95 (1 H, dd, *J* 2.44 and 12.82) and 7.44–7.47 (5 H, m); δ_C(100 MHz; $CDCl_3$; Me_4Si) 22.6, 23.3, 23.9, 32.4, 40.8, 58.8, 128.3 (2 C), 129.9 (2 C), 130.4 and 133.0.

Reaction of salt 3 with $NaNH_2$ in liquid NH_3

(**A**). Salt **3** (690 mg, 2.0 mmol) was added portionwise to a solution of $NaNH_2$ [from Na metal (70 mg, 3.0 mmol)] in liquid NH_3 (20 cm^3, NH_3 vapour condensed in dry air), and the mixture was stirred for 3 h. NH_4Cl (109 mg, 2.0 mmol) was added to the mixture and NH_3 was evaporated off. Water (20 cm^3) was added to the residue, and the mixture was extracted with Et_2O. The ethereal extract was dried ($MgSO_4$), and concentrated under reduced pressure to give 5-*methylsulfanyl*-1-*phenylpentan*-1-*one* **4** (236 mg, 57%) as an oil, bp 100 °C (2 mmHg) (Found: C, 69.1; H, 7.8. $C_{12}H_{16}OS$ requires C, 69.2; H, 7.7%); ν_{max}(KBr)/cm^{-1} 2949, 2915 and 1680; δ_H(500 MHz; $CDCl_3$; Me_4Si) 1.70 (2 H, m), 1.86 (2 H, m), 2.10 (3 H, s), 2.55 (2 H, t, *J* 7.3), 3.00 (2 H, t, *J* 7.3), 7.46 (2 H, m), 7.56 (1 H, m) and 7.95 (2 H, m); δ_C(125 MHz; $CDCl_3$; Me_4Si) 15.5, 23.4, 28.7, 34.0, 38.0, 128.0 (2 C), 128.6 (2 C), 133.0, 137.0 and 199.9; *m*/*z* 210 (M^+ + 2, 2%), 209 (M^+ + 1, 8), 208 (M^+, 23), 161 (64), 105 (100), 77 (76) and 61 (20).

(**B**). The same reaction was carried out under N_2 and worked up to give 1,3,4,5,6,11a-hexahydro-7*E*-2-benzothionine **5** (499 mg, 62%), a non-distillable oil; δ_H(270 MHz; $CDCl_3$; Me_4Si) 1.60–1.78 (4 H, m), 1.91 (1 H, dd, *J* 10.7 and 14.2), 1.98–2.09 (1 H, m), 2.36–2.69 (4 H, m), 2.88 (1 H, dd, *J* 4.3 and 14.2), 5.72 (1 H, m), 5.95 (1 H, m), 6.11 (2 H, m) and 6.49 (1 H, d, *J* 9.6); δ_C(125 MHz; $CDCl_3$; Me_4Si) 25.8, 26.1, 27.2, 35.2, 40.8, 47.1, 121.8, 123.05, 123.8, 130.2 and 132.9 (2 C); λ_{max}(MeCN)/nm 315 (log ε dm^3 mol^{-1} cm^{-1} 3.9).

trans-2-Phenyl-1-[(trimethylsilyl)methyl]tetrahydrothiopyranium perchlorate (*trans*-7)

(Trimethylsilyl)methyl triflate (7.10 g, 30.0 mmol) was added to a solution of compound **6** (3.62 g, 20.3 mmol) in CH_2Cl_2 (20 cm^3) at rt. The mixture was stirred for 3 h and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (10 cm^3) and the solution was stirred with aq. $NaClO_4$ (7.93 g, 64.7 mmol in 40 cm^3) overnight. The CH_2Cl_2 layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined CH_2Cl_2 layers were dried ($MgSO_4$), and concentrated under reduced pressure, and the residue was recrystallized from ethyl acetate to give the *title salt* trans-**7** (6.34 g, 86%), mp 121–122 °C (Found: C, 49.1; H, 6.9. $C_{15}H_{25}ClO_4SSi$ requires C, 49.4; H, 6.9%); ν_{max}(KBr)/cm^{-1} 2946, 1445, 1256, 1088 and 851; δ_H(270 MHz; $CDCl_3$; Me_4Si) 0.13 (9 H, s), 1.93 (1 H, AB-q, *J* 13.9), 2.05–2.25 (4 H, m), 2.43 (2 H, d, *J* 14.8), 3.01 (1 H, AB-q, *J* 13.9), 3.50 (1 H, m), 3.82 (1 H, m), 4.95 (1 H, dd, *J* 3.0 and 11.9) and 7.43–7.49 (5 H, m).

Reaction of the salt *trans*-7 with CsF

(Entries 1 and 2 in Table 1). CsF (0.62 g, 4.1 mmol) was added to a solution of the salt *trans*-**7** (0.73 g, 2.0 mmol) in DME (10 cm^3) under N_2 and the mixture was stirred at 0 °C for 3 or 24 h. The mixture was poured into water and extracted with Et_2O. The ethereal extract was dried ($MgSO_4$), and concentrated under reduced pressure to give a mixture of products **4**, **5**, **6** and (E)-5-*methylsulfanyl*-1-*phenylpent*-1-*ene* **11** (after 3 h, total 204 mg, 54%, proportions 0 : 75 : 21 : 4; after 24 h, total yield 139 mg, 37%, proportions 2 : 55 : 29 : 14). Isolation of each compound was difficult due to insufficient separation on silica gel columns. The product proportions were determined by integration of the ^1H signals at 400 MHz in the NMR spectra of the mixture.

Compound **11**: δ_H(400 MHz; $CDCl_3$; Me_4Si) 1.74–1.80 (2 H, m), 2.10 (3 H, s), 2.29–2.34 (2 H, m), 2.53 (2 H, t, *J* 7.3), 6.19 (1 H, dt, *J* 15.8 and 7.3), 6.40 (1 H, d, *J* 15.8) and 7.17–7.35 (5 H, m); δ_C(125 MHz; $CDCl_3$; Me_4Si) 15.5, 28.7, 32.0, 33.7, 126.0 (2 C), 127.0, 128.5 (2 C), 129.7, 130.6 and 137.6; *m*/*z* (GC-EI) 192.0961 (M^+. $C_{12}H_{16}S$ requires *M*, 192.0973), 194 (M^+ + 2, 3%), 193 (M^+ + 1, 9), 192 (M^+, 62), 144 (52), 129 (100), 115 (35) and 91 (28).

(Entry 3). The same reaction was carried out at rt for 24 h to give a mixture of products **4**, **5**, **6**, **11** and **12** (total yield 246 mg, 45%, proportions 2 : 38 : 15 : 43 : 2).

(Entry 4). The same reaction was carried out at 70 °C for 24 h and the product worked up to give compound **11** (328 mg, 85%).

(Entries 5 and 6). CsF (0.62 g, 4.1 mmol) was added to a solution of the salt *trans*-**7** (0.73 g, 2.0 mmol) and DBU (0.61 g,

† 1 cal = 4.184 J.

4.0 mmol) in DME (10 cm^3) at 0 or 25 °C and the mixture was stirred for 24 h and worked up to give a mixture of products **4**, **5**, **6**, **11** and **12** (at 0 °C, total yield 157 mg, 41%, proportions 6 : 59 : 13 : 13 : 9; at 25 °C, total yield 348 mg, 93%, proportions 0 : 9 : 38 : 37 : 16).

(Entry 7). The same mixture of salt *trans*-**7** and CsF in DME described for entries 1 and 2 was stirred in dry air at rt for 3 h and worked up to give a complex mixture which was difficult to separate.

(Entry 8). The same mixture of salt *trans*-**7**, CsF and DBU described for entry 6 was stirred in air for 3 h and worked up to give a mixture of compounds **4**, **5**, **6**, **11** and **12** (total yield 203 mg, 54%, proportions 4 : 20 : 34 : 36 : 6).

(Entries 9 and 10). CsF (0.62 g, 4.1 mmol) was added to a solution of salt *trans*-**7** (0.73 g, 2.0 mmol) in DMSO (10 cm^3) and the mixture was stirred at rt for 3 or 24 h under N_2 and was then worked up to give a mixture of compounds **4**, **5**, **6**, **11** and **12** (after 3 h, total yield 256 mg, 67%, proportions 0 : 67 : 0 : 28 : 5; after 24 h, total yield 199 mg, 47%, proportions 11 : 17 : 15 : 38 : 19).

(Entry 11). CsF (0.62 g, 4.1 mmol) was added to a solution of salt *trans*-**7** (0.73 g, 2.0 mmol) and DBU (0.61 g, 4.0 mmol) in DMSO (10 cm^3) at rt under N_2 and the mixture was stirred for 24 h and then worked up to give a mixture of compounds **4**, **6**, **11** and **12** (total yield 290 mg, 77%, proportions 1 : 24 : 25 : 50).

Change of bicycle 5 in DME

(Entry 1 in Table 2). A solution of compound **5** (132 mg, 0.686 mmol) in DME (5 cm^3) was stirred at rt under N_2 for 20 h. The mixture was poured into water (40 cm^3) and extracted with Et_2O. The extract was dried ($MgSO_4$) and concentrated to recover starting material **5** (112 mg, 85%).

(Entries 2 and 3). To a solution of compound **5** (269 mg, 1.40 mmol) in DME (5 cm^3) was added DBU (426 mg, 2.80 mmol) under N_2 and the mixture was stirred at rt for 20 or 72 h and then worked up in a manner similar to that described above to give a mixture of starting material **5** and isomer **12** (total 250 mg, 93%, ratio 35 : 65) after 20 h, and to give almost pure isomer **12** (257 mg, 96%) after 72 h.

Compound **12**: bp 115–120 °C (1.3 mmHg), mp 50–51 °C (Found: C, 74.8; H, 8.5. $C_{12}H_{16}S$ requires C, 74.9; H, 8.4%); ν_{max}(KBr)/cm^{-1} 2922, 1443 and 754; δ_H(500 MHz; $CDCl_3$; Me_4Si) 1.35–1.42 (2 H, m), 1.62–1.68 (2 H, m), 1.76–1.82 (2 H, m), 2.70–2.75 (4 H, m), 3.80 (2 H, s) and 7.12–7.22 (4 H, m); δ_C(125 MHz; $CDCl_3$; Me_4Si) 21.5, 30.9, 31.7, 32.6, 33.6, 36.8, 126.5, 127.2, 129.5, 129.7, 139.5 and 140.9; *m*/*z* 194 (M^+ + 2, 6%), 193 (M^+ + 1, 14), 192 (M^+, 100), 143 (43), 131 (31), 115 (32), 104 (45) and 87 (91).

(Entry 4). A solution of compound **5** (266 mg, 1.383 mmol) in DMSO (5 cm^3) was stirred at rt under N_2 for 20 h. The mixture was treated in a manner similar to that described above to give a mixture of starting material **5** and isomer **12** (total 222 mg, 83%, ratio 44 : 56).

Change of bicycle 5 in a KOH–EtOH solution

(Entry 5 in Table 2). To a solution of 10% KOH in EtOH (10 cm^3) was added bicycle **5** (0.499 g, 2.59 mmol), and the mixture was stirred at rt for 24 h. The mixture was mixed with water (50 cm^3), extracted with Et_2O, and the extract was dried ($MgSO_4$) and concentrated to give a mixture of compounds **6**, **11** and **12** (total yield 375 mg, 77%, proportions 30 : 51 : 19). The product proportion were determined by integration of the ^1H signals at 500 MHz in the NMR spectra.

Reaction of bicycle 5 with benzaldehyde

A solution of compound **5** (328 mg, 1.71 mmol) and benzaldehyde (181 mg, 1.71 mmol) in DME (5 cm^3) was stirred at rt for 20 h under N_2. The mixture was mixed with water and extracted with Et_2O. The extract was dried ($MgSO_4$) and concentrated to give a mixture of starting material **5**, isomer **6** and phenyloxirane **14** (total 368 mg, **5** 0.78 mmol, **6** 0.84 mmol, **14** 0.81 mmol). The structure of compound **14** was confirmed by comparison with an authentic sample by GLC-MS and ^1H NMR spectra. Mole ratios of the products were determined by integration of the ^1H signals at 500 MHz.

Computational methods

Starting geometries for the calculations were obtained with MOL-MOLIS (Daikin Industries, Ltd., Shinjiku-ku, Tokyo, Japan). Calculations for salt **7** were performed at the restricted Hartree–Fock (RHF) level with the AM1 method[10] in the MOPAC 93 program.[11] Geometries were optimized with the Eigenvector Following routine. Calculations for ylides **8** and **9** were carried out using the GAUSSIAN 94 package.[12] Geometries for ylides **8** and **9** were initially optimized at the HF/3-21G* level.[13] Finally, further geometry optimizations were performed using the Becke3LYP/6-31G* level.[8]

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Paper 8/02309C
Received 24*th March* 1998
Accepted 12*th May* 1998