[Chem. Pharm. Bull. 34(9)3682—3687(1986)]

Sigmatropic Rearrangement of Cyclic α-Vinyl Sulfonium Imides: Formation of Thiazocine, Thiazonine, and Thiazecine Derivatives[1)]

HARUKI SASHIDA and TAKASHI TSUCHIYA*

School of Pharmacy, Hokuriku University, Kanagawa-machi, Kanazawa 920–11, Japan

(Received March 4, 1986)

Thermolysis of the cyclic α-vinyl sulfonium *p*-toluenesulfonylimides (**6a**—**c**), prepared from 2-vinylthiolane (**5a**), 2-vinylthiane (**5b**), and 2-vinylthiepane (**5c**) by treatment with chloramine T, resulted in [2,3]-sigmatropic rearrangement with ring-expansion to give the 1,2-thiazocine (**7a**), 1,2-thiazonine (**7b**), and 1,2-thiazecine derivative (**7c**), respectively. Similarly, the 1,2-benzothiazonine (**17**) and the 3,4-benzothiazonine (**18**) were obtained from 2-vinylthiochroman (**13**) and 1-vinylisothiochroman (**14**) *via* the imides (**15** and **16**), respectively. The stereochemistry of the rearrangement is discussed.

Keywords——sigmatropic rearrangement; thermolysis; ring-expansion; cyclic sulfonium imide; cyclic 2-vinyl sulfide; 1,2-thiazocine; 1,2-thiazonine; 1,2-thiazecine; benzothiazonine

Thermal sigmatropic rearrangements of cyclic allylamine *N*-ylides (**1**) have been well studied in connection with those of related open-chain compounds.[2)] The allylamine *N*-ylides (**1a**)[3)] and *N*-imides (**1b**)[4)] are known to undergo [2,3]-sigmatropic rearrangement to give the corresponding ring-expansion products, while in contrast, the thermolysis of the allylamine *N*-oxides (**1c**)[5)] results in Meisenheimer-type [1,2] rearrangement predominantly and no [2,3]-sigmatropic rearrangement. The 2-vinyl (**2a**)[3,6)] and 2-ethynyl cyclic sulfonium ylides (**2b**)[1,7)] also undergo the thermal [2,3]rearrangement. As regards sulfonium imides, Tamura *et al.*[8)] have reported that treatment of the thiochroman-4-one *S*-imides (**3**) affords tetrahydro-1,2-benzothiazepin-5-one derivatives by a novel rearrangement *via* Hofmann elimination followed by cyclization. However, no sigmatropic rearrangement has been reported for cyclic sulfonium imides, although open-chain allyl sulfonium imides are known to undergo [2,3]-sigmatropic rearrangement.[9)] Therefore, we were interested in the thermal behavior of the cyclic allyl sulfonium imides (**4**) and report here our new results.[10)]

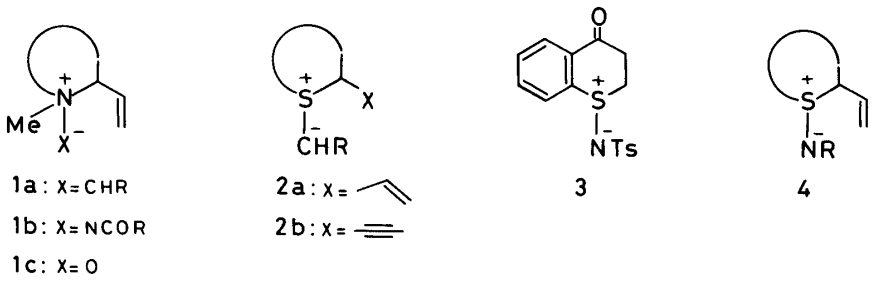

Chart 1

The cyclic 2-vinyl sulfides (**5a**—**c**) were prepared from the corresponding five-, six-, and seven-membered thiacycloalkanes by successive treatment with *N*-chlorosuccinimide and vinylmagnesium bromide, according to the reported method.[3,6)]

Treatment of 2-vinylthiolane (**5a**) and 2-vinylthiane (**5b**) with sodium *p*-toluenesulfonchloramide (chloramine T) trihydrate[8] in methanol at room temperature gave the corresponding *p*-toluenesulfonylimides (**6a**: 70% yield) and (**6b**: 61% yield), respectively. In each case, only one diastereomer of the *S*-imide was isolated and no evidence for a second isomer could be found. Thermolysis of the *S*-imides **6a** and **6b** in xylene at *ca.* 140 °C for 3 h resulted in ring-expansion to give the 1,2-thiazocine (**7a**: 55% yield) and 1,2-thiazonine (**7b**: 54% yield) as the sole products, respectively.

The thermal behavior of the seven-membered ring compound was somewhat different from that of five- and six-membered ring compounds. 2-Vinylthiepane (**5c**), upon treatment with chloramine T at room temperature, afforded directly the ring-expansion product, the 1,2-thiazecine derivative (**7c**), in 61% yield, and the *S*-imide (**6c**) could not be isolated even when the reaction was carried out at *ca.* 0 °C. This result indicates that the rearrangement of the seven-membered ring *S*-imide **6c** occurs readily at room temperature or below.

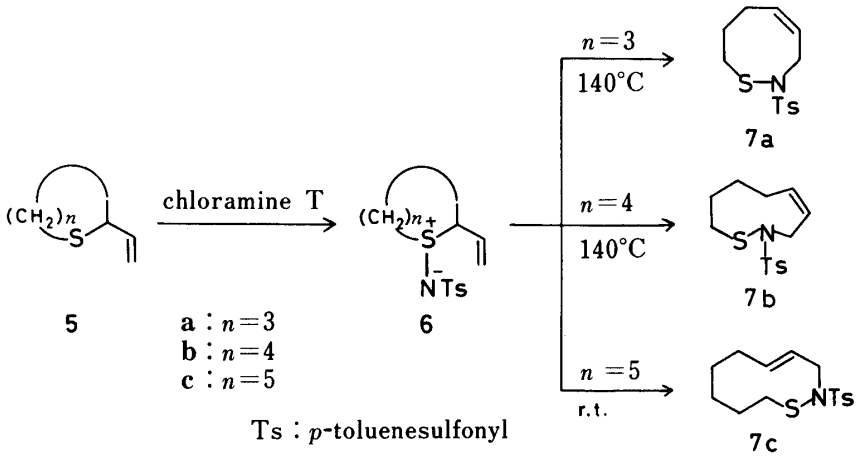

Chart 2

The structures of **7** thus obtained were characterized by elemental and spectral analyses. On the basis of the vicinal coupling constants of the olefinic protons in **7** observed by proton nuclear magnetic resonance (^{1}H-NMR) decoupling studies, both **7a** and **7b** were shown to have a *cis* double bond ($J_{4,5}=10$ Hz), while the double bond in **7c** was proved to be *trans* ($J_{4,5}=15$ Hz). No thermal *cis*↔*trans* geometorical isomerization was observed for any of the ring-expansion products **7**; this fact shows that the rearrangement occurs stereoselectively.

The above results clearly indicate that this ring-expansion reaction proceeds *via* [2,3]-sigmatropic rearrangement, analogous to the cases of the cyclic allyl amine *N*-ylides (**1**)[3,4,11] and sulfide *S*-ylides (**2**).[3,6] The alkylation of cyclic sulfides is well known to occur by least-hindered approach of alkylating reagents.[12] Thus, it seems clear that the *S*-imination of **5** with chloramine T also occurs in a similar manner and the resulting imides as the sole products have *trans* stereochemistry as indicated in the stereo-structures **6a**—**c** shown in Chart 3, although specific evidence to confirm this is not available.

In the case of the five-membered-ring *S*-imide **6a**, the thermolysis may proceed by initial thermal pyramidal inversion[13] to the *cis* diastereomer **8**, which then undergoes rearrangement to give **7a** having a *cis* double bond *via* the bonded transition state **9**, analogous to the case of the 2-vinylthiolane *S*-ylides.[3,6] The six-membered-ring *S*-imide **6b** may also rearrange to the product **7b** with a *cis* double bond *via* the *cis* diastereomer (**10**) and the transition state (**11**). This result is different from that with the 2-vinylthiane *S*-ylides, which afford the ring-expansion products having a *trans* double bond.[3,6] The rearrangement of the *S*-ylides readily takes place below room temperature, and therefore the initially formed diequatorial

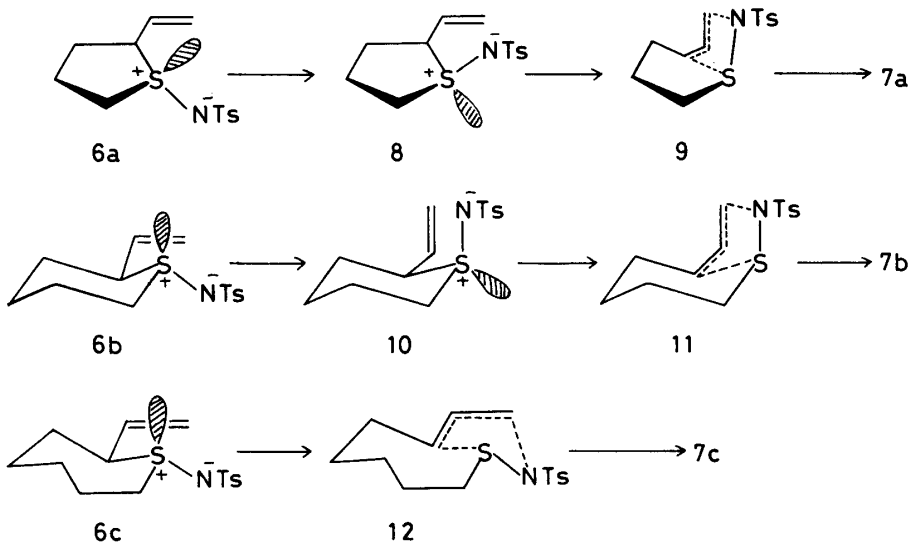

Chart 3

conformer of the *S*-ylides rearranges directly without pyramidal inversion to result in the formation of the *trans* products. In contrast, the rearrangement of the present *S*-imide **6b** did not occur below 110 °C. This fact shows that the diequatorial conformer **6b** shown in Chart 3 can not undergo the rearrangement, which thus may occur *via* the axial imide isomer **10** converted by thermal pyramidal inversion to the thermodynamically stable *cis* product **7b**.[14] In the case of the seven-membered-ring *S*-imide, the *trans* diastereomer **6c** might be susceptible to the rearrangement because the ring is somewhat flexible conformationally, and thus the reaction occurs at room temperature or below without pyramidal inversion; consequently the product has a *trans* geometry.

Next, this ring-expansion reaction was applied to some benzo-derivatives. 2-Vinylthiochroman (**13**) and 1-vinylisothiochroman (**14**) were prepared from thiochroman and isothiochroman, respectively, by successive treatment with *N*-chlorosuccinimide and vinylmagnesium bromide in 65%—75% yields. Treatment of **13** and **14** with chloramine T in methanol at room temperature gave the *p*-toluenesulfonyl imides (**15** and **16**) in yields of 70% and 83%, respectively. Heating the imides **15** and **16** at 140 °C in xylene resulted in ring-expansion to give the 1,2-benzothiazonine (**17**) and 3,4-benzothiazonine (**18**) derivatives in yields of 55% and 57%, respectively. The double bonds in both **17** and **18** were proved to be *cis* by ^{1}H-NMR spectral analyses.

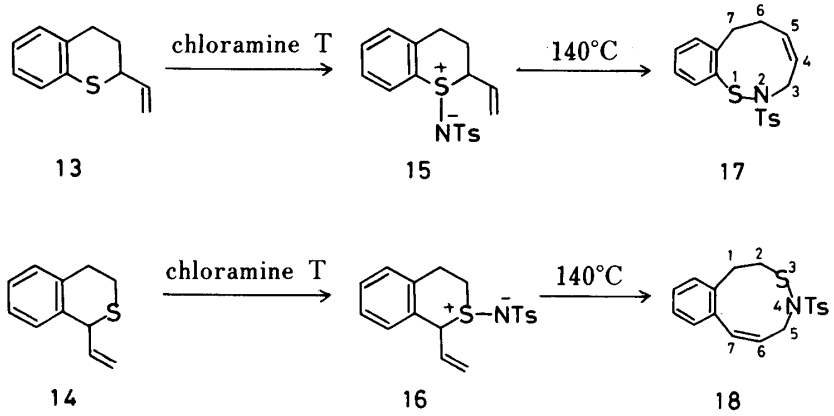

Chart 4

In conclusion, all of the ring-expansion products reported are novel ring systems and the present results provide a synthetic method for preparing 1,2-thiaza medium-sized rings, although the fully unsaturated compounds have not yet been synthesized.

Experimental

Melting points were measured on a Yanagimoto micro melting point hot stage apparatus and are uncorrected. Infrared (IR) spectra were determined with a Hitachi 270-30 spectrometer and mass spectra (MS) were recorded on a JEOL DX-300 instrument. ^{1}H-NMR spectra were recorded on a JEOL JNM-MH100 spectrometer in $CDCl_3$ using tetramethylsilane as an internal standard unless otherwise stated; spectral assignments were confirmed by spin-decoupling experiments. Microanalyses were performed in the Microanalytical Laboratory of this school by Mrs. R. Igarashi.

Starting Materials——The cyclic 2-vinyl sulfides (**5a—c**),[3,6] thiochroman,[15] and isothiochroman[16] were prepared by the reported methods.

2-Vinylthiolane *S*-(*p*-Toluenesulfonyl)imide (6a)——A mixture of 2-vinylthiolane (**5a**: 1.14 g, 10 mmol), chloramine T trihydrate (3.38 g, 12 mmol), and methanol (20 ml) was stirred for 5 h at room temperature and then concentrated *in vacuo*. The residue was chromatographed on silica gel using CH_2Cl_2–MeOH (100 : 1) as an eluent to give **6a**: 1.96 g, 70% yield, mp 113—115 °C, colorless prisms (from acetone–ether). MS *m/z*: 283 (M^+). IR ν_{max}^{KBr} cm^{-1}: 1140, 1270 (SO_2). NMR δ: 1.8—2.6 (4H, m, 3- and 4-H_2), 2.36 (3H, s, Ph-Me), 2.8—3.3 (2H, m, 5-H_2), 3.9 (1H, m, 2-H), 5.08 (1H, d, J=10 Hz, –CH=C$\underline{H}_2$ *cis*), 5.09 (1H, d, J=17 Hz, –CH=C$\underline{H}_2$ *trans*), 5.69 (1H, ddd, J=17, 10, 7 Hz, –C$\underline{H}$=CH$_2$), 7.17, 7.67 (each 2H, d, J=8 Hz, Ph-H). *Anal.* Calcd for $C_{13}H_{17}NO_2S_2$: C, 55.12; H, 6.00; N, 4.97. Found: C, 55.04; H, 6.12; N, 4.98.

2-Vinylthiane *S*-(*p*-Toluenesulfonyl)imide (6b)——2-Vinylthiane (**5b**: 1.28 g, 10 mmol) was treated with chloramine T and worked up as described for **6a** to give **6b**; 1.81 g, 61% yield, mp 91—93 °C, colorless prisms (from acetone–ether). MS *m/z*: 297 (M^+). IR ν_{max}^{KBr} cm^{-1}: 1140, 1280 (SO_2). NMR δ: 1.4—2.4 (6H, m, 3-, 4-, and 5-H_2), 2.38 (3H, s, Ph-Me), 2.7—3.3 (2H, m, 6-H_2), 3.5 (1H, m, 2-H), 5.17 (1H, dd, J=10, 1 Hz, –CH=C$\underline{H}_2$ *cis*), 5.30 (1H, dd, J=17, 1 Hz, –CH=C$\underline{H}_2$ *trans*), 5.60 (1H, ddd, J=17, 10, 7 Hz, –C$\underline{H}$=CH$_2$), 7.19, 7.69 (each 2H, d, J=8 Hz, Ph-H). *Anal.* Calcd for $C_{14}H_{19}NO_2S_2$: C, 56.56; H, 6.40; N, 4.71. Found: C, 56.18; H, 6.33; N, 4.68.

2-(*p*-Toluenesulfonyl)-2,3,6,7-tetrahydro-8*H*-1,2-thiazocine (7a)——A solution of the *S*-imide (**6a**: 566 mg, 2 mmol) in xylene (10 ml) was heated under reflux with stirring for 3 h. After cooling, the solvent was removed *in vacuo* and the residue was chromatographed on silica gel using CH_2Cl_2 as an eluent to give **7a**: 311 mg, 55% yield, mp 68—69 °C, colorless prisms (benzene–*n*-hexane). MS *m/z*: 283 (M^+). IR ν_{max}^{KBr} cm^{-1}: 1150, 1340 (SO_2). NMR δ: 1.95 (2H, m, 7-H_2), 2.40 (3H, s, Ph-Me), 2.5 (2H, m, 6-H_2), 2.83 (2H, t, J=6 Hz, 8-H_2), 4.16 (2H, d, J=6 Hz, 3-H_2), 5.8—6.0 (2H, m, 4- and 5-H), 7.26, 7.76 (each 2H, d, J=8 Hz, Ph-H); irradiation at 4.16: 5.86 (1H, dt, J=10, 7 Hz, 5-H), 5.98 (1H, d, J=10 Hz, 4-H). *Anal.* Calcd for $C_{13}H_{17}NO_2S_2$: C, 55.12; H, 6.01; N, 4.95. Found: C, 54.98; H, 6.00; N, 4.88.

2-(*p*-Toluenesulfonyl)-2,3,6,7,8,9-hexahydro-1,2-thiazonine (7b)——A solution of the *S*-imide (**6b**: 594 mg, 2 mmol) in xylene (10 ml) was heated and worked up as described for **7a** to give **7b**: 320 mg, 54% yield, mp 54—56 °C, colorless prisms (from benzene–*n*-hexane). MS *m/z*: 297 (M^+). IR ν_{max}^{KBr} cm^{-1}: 1160, 1350 (SO_2). NMR δ: 1.5—2.0 (4H, m, 7- and 8-H_2), 2.39 (3H, s, Ph-Me), 2.6 (2H, m, 6-H_2), 2.9—3.0 (2H, m, 9-H_2), 3.86 (2H, d, J=6 Hz, 3-H_2), 5.8—5.9 (2H, m, 4- and 5-H), 7.26, 7.76 (each 2H, d, J=8 Hz, Ph-H); irradiation at 3.86: 5.71 (1H, dt, J=10, 6 Hz, 5-H), 5.87 (1H, d, J=10 Hz, 4-H). *Anal.* Calcd for $C_{14}H_{19}NO_2S_2$: C, 56.57; H, 6.40; N, 4.71. Found: C, 56.54; H, 6.46; N, 4.71.

2-(*p*-Toluenesulfonyl)-2,3,6,7,8,9-hexahydro-10*H*-1,2-thiazecine (7c)——A mixture of 2-vinylthiepane (**5c**: 1.42 g, 10 mmol), chloramine T trihydrate (3.38 g, 12 mmol), and methanol (20 ml) was stirred for 5 h at room temperature and then concentrated *in vacuo*. The residue was chromatographed on silica gel using CH_2Cl_2 as an eluent to give **7c**: 1.89 g, 61% yield, mp 123—124 °C, colorless prisms (from benzene–*n*-hexane). MS *m/z*: 311 (M^+). IR ν_{max}^{KBr} cm^{-1}: 1165, 1345 (SO_2). NMR δ: 1.2—1.8 (6H, m, 7-, 8-, and 9-H_2), 2.2 (2H, m, 6-H_2), 2.39 (3H, s, Ph-Me), 2.4—4.4 (4H, m, 3- and 10-H_2), 5.42 (1H, dt, J=15, 7 Hz, 5-H), 5.73 (1H, dt, J=15, 7 Hz, 4-H), 7.25, 7.77 (each 2H, d, J=8 Hz, Ph-H). *Anal.* Calcd for $C_{15}H_{21}NO_2S_2$: C, 57.88; H, 6.76; N, 4.50. Found: C, 57.76; H, 6.76; N, 4.45.

2-Vinylthiochroman (13)——*N*-Chlorosuccinimide (NCS: 6.75 g, 50 mmol) was added in small portions over a 30 min period to a solution of thiochroman (7.50 g, 50 mmol) in benzene (100 ml) with stirring below 5 °C in an ice bath. The reaction mixture was stirred for a further 1 h and then the resulting precipitate of succinimide was removed by filtration. The benzene solution (containing 2-chlorothiochroman) was added under N_2 at below 10 °C to a tetrahydrofuran (100 ml) solution of vinylmagnesium bromide, which was freshly prepared from vinyl bromide (9.63 g, 90 mmol) and magnesium (2.19 g, 90 mmol) under N_2 in an ice bath. The reaction mixture was stirred for an additional 1 h below 10 °C and then diluted with 10% H_2SO_4 (100 ml). After separation of the layers, the aqueous layer was extracted with ether. The combined organic layer was successively washed with satd. $NaHCO_3$ and satd. NaCl, dried over $MgSO_4$, and evaporated *in vacuo*. The residue was chromatographed on silica gel using *n*-

hexane–CH_2Cl_2 (5 : 1) as an eluent to give **13**: 6.53 g, 74% yield, colorless oil. MS *m/z*: 176 (M^+). NMR δ: 1.5—2.2 (2H, m, 3-H_2), 2.5—2.8 (2H, m, 4-H_2), 3.69 (1H, dt, J=5, 9 Hz, 2-H), 4.95 (1H, d, J=10 Hz, –CH=C$\underline{H}_2$ *cis*), 5.09 (1H, d, J=17 Hz, –CH=C$\underline{H}_2$ *trans*), 5.72 (1H, ddd, J=17, 10, 8 Hz, –C$\underline{H}$=CH_2), 6.7—7.0 (4H, m, Ph-H). *Anal.* Calcd for $C_{11}H_{12}S$: C, 75.00; H, 6.82. Found: C, 75.29; H, 6.98.

1-Vinylisothiochroman (14)——Isothiochroman (7.50 g, 50 mmol) was successively treated with NCS and vinylmagnesium bromide, and worked up as described for **13** to give **14**: 5.72 g 65% yield, colorless oil. MS *m/z*: 176 (M^+). NMR δ: 2.8—3.1 (4H, m, 3- and 4-H_2), 4.47 (1H, d, J=7 Hz, 1-H), 4.88 (1H, dd, J=17, 1 Hz, –CH=C$\underline{H}_2$ *trans*), 5.06 (1H, dd, J=10, 1 Hz, –CH=C$\underline{H}_2$ *cis*), 6.07 (1H, ddd, J=17, 10, 7 Hz, –C$\underline{H}$=CH_2), 7.0—7.3 (4H, m, Ph-H). *Anal.* Calcd for $C_{11}H_{12}S$: C, 75.00; H, 6.82. Found: C, 74.71; H, 6.83.

2-Vinylthiochroman *S*-(*p*-Toluenesulfonyl)imide (15)——A mixture of **13** (0.88 g, 5 mmol), chloramine T trihydrate (1.46 g, 5.2 mmol), and methanol (10 ml) was stirred for 2 h at room temperature and then concentrated *in vacuo* below 30 °C. The residue was extracted with CH_2Cl_2 and the extract was washed with satd. NaCl, dried, and evaporated to dryness *in vacuo* below 30 °C. The resulting crystalline residue was washed with ether and recrystallized from ether–acetone to give **15**: 1.20 g, 70% yield, mp 97—100 °C, colorless prisms. MS *m/z*: 345 (M^+). IR ν_{max}^{KBr} cm^{-1}: 1140, 1280 (SO_2). NMR δ: 2.47 (3H, s, Ph-Me), 2.0—2.8 (2H, m, 3-H_2), 3.0—3.4 (2H, m, 4-H_2), 3.95 (1H, dt, J=8, 7 Hz, 2-H), 5.32 (1H, dd, J=10, 1 Hz, –CH=C$\underline{H}_2$ *cis*), 5.48 (1H, dd, J=17, 1 Hz, –CH=C$\underline{H}_2$ *trans*), 5.76 (1H, ddd, J=17, 10, 8 Hz, –C$\underline{H}$=CH_2), 7.3—7.8 and 7.9—8.1 (6H, m, and 2H, m, Ph-H). *Anal.* Calcd for $C_{18}H_{19}NO_2S_2$: C, 62.61; H, 5.51; N, 4.06. Found: C, 62.62; H, 5.79; N, 3.90.

1-Vinylisothiochroman *S*-(*p*-Toluenesulfonyl)imide (16)——1-Vinylisothiochroman (**14**: 0.88 g, 5 mmol) was trated with chloramine T trihydrate (1.46 g, 5.2 mmol) and worked up as described for **15** to give **16**, which was too hygroscopic to be purified and thus was used in the following reaction without further purification. Crude **16**: 1.43 g, 83% yield. NMR δ: 2.34 (3H, s, Ph-Me), 2.7—4.2 (4H, m, 3- and 4-H_2), 4.64 (1H, d, J=8 Hz, 1-H), 5.22 (1H, d, J=17 Hz, –CH=C$\underline{H}_2$ *trans*), 5.35 (1H, d, J=10 Hz, –CH=C$\underline{H}_2$ *cis*), 5.6—6.0 (1H, m, –C$\underline{H}$=CH_2), 6.9—7.4 and 7.6—7.8 (6H, m, and 2H, m, Ph-H).

2-(*p*-Toluenesulfonyl)-2,3,6,7-tetrahydro-1,2-benzothiazonine (17)——A solution of **15** (690 mg, 2 mmol) in xylene was heated and worked up as described for **7a** to give **17**: 380 mg, 55% yield, mp 92—93 °C, colorless prisms (from CH_2Cl_2–*n*-hexane). MS *m/z*: 345 (M^+). IR ν_{max}^{KBr} cm^{-1}: 1160, 1350 (SO_2). NMR δ: 2.43 (3H, s, Ph-Me), 2.5—2.8 (2H, m, 6-H_2), 3.0—3.3 (2H, m, 7-H_2), 3.95 (2H, d, J=8 Hz, 3-H_2), 5.51 (1H, dt, J=10, 8 Hz, 5-H), 5.73 (1H, dt, J=10, 8 Hz, 4-H), 7.1—7.5 and 7.7—7.9 (6H, m, and 2H, m, Ph-H). *Anal.* Calcd for $C_{18}H_{19}NO_2S_2$: C, 62.61; H, 5.51; N, 4.06. Found: C, 62.39; H, 5.40; N, 3.97.

4-(*p*-Toluenesulfonyl)-1,2,4,5-tetrahydro-3,4-benzothiazonine (18)——A solution of **16** (690 mg, 2 mmol) in xylene was heated and worked up as described for **7a** to give **18**: 393 mg, 57% yield, mp 185—187 °C, colorless prisms (from CH_2Cl_2–*n*-hexane). MS *m/z*: 345 (M^+). IR ν_{max}^{KBr} cm^{-1}: 1160, 1340 (SO_2). NMR δ: 2.33 (3H, s, Ph-Me), 2.7—3.2 (4H, m, 1- and 2-H_2), 3.56 (2H, d, J=7 Hz, 5-H_2), 6.09 (1H, dt, J=10, 7 Hz, 6-H), 6.68 (1H, d, J=10 Hz, 7-H), 6.7—7.2 and 7.57 (6H, m, and 2H, d, J=7 Hz, Ph-H). *Anal.* Calcd for $C_{18}H_{19}NO_2S_2$: C, 62.61; H, 5.51; N, 4.06. Found: C, 62.83; H, 5.34; N, 4.08.

References and Notes

1) This paper constitutes Part VII in the series "Thermal Rearrangements of Cyclic Amine Ylides"; Part VI: H. Sashida and T. Tsuchiya, *Chem. Pharm. Bull.*, **34**, 3644 (1986).
2) For reviews, see W. J. McKillip, E. A. Sedor, B. M. Culbertson, and S. Wawzonek, *Chem. Rev.*, **73**, 255 (1973); T. L. Gilchrist and C. J. Moody, *ibid.*, **77**, 409 (1977); E. C. Taylor and I. J. Turchi, *ibid.*, **79**, 181 (1979); T. Hayashi, *Yuki Gosei Kagaku Kyokai Shi*, **34**, 396 (1976); T. Nakai and K. Mikami, *ibid.*, **38**, 381 (1980).
3) E. Vedejs, M. J. Arco, D. W. Powell, J. M. Renga, and S. P. Singer, *J. Org. Chem.*, **43**, 4831 (1978).
4) T. Tsuchiya and H. Sashida, *Heterocycles*, **12**, 1453 (1979); *idem, Chem. Pharm. Bull.*, **29**, 1887 (1981).
5) T. Tsuchiya and H. Sashida, *Heterocycles*, **14**, 1925 (1980); H. Sashida and T. Tsuchiya, *Chem. Pharm. Bull.*, **32**, 4117 (1984).
6) E. Vedejs and J. P. Hagen, *J. Am. Chem. Soc.*, **97**, 6878 (1975); E. Vedejs, J. P. Hagen, B. L. Roach, and K. L. Spear, *J. Org. Chem.*, **43**, 1185 (1978); V. Ceré, C. Paolucci, S. Pollicino, E. Sandri, A. Fava, and L. Lunazzi, *ibid.*, **45**, 3613 (1980).
7) H. Sashida and T. Tsuchiya, *Heterocycles*, **19**, 2147 (1982).
8) Y. Tamura, S. M. Bayomi, C. Mukai, M. Ikeda, M. Murase, and M. Kise, *Tetrahedron Lett.*, **1980**, 533; Y. Tamura, Y. Takebe, S. M. Bayomi, C. Mukai, M. Ikeda, M. Murase, and M. Kise, *J. Chem. Soc., Perkin Trans. 1*, **1981**, 1037.
9) A. S. F. Ash, F. Challenger, T. S. Stevens, and J. L. Dunn, *J. Chem. Soc.*, **1952**, 2792; Y. Tamura, H. Matsushima, J. Minamikawa, M. Ikeda, and K. Sumoto, *Tetrahedron*, **31**, 3035 (1975).
10) A part of this work has been published in a preliminary communication: H. Sashida and T. Tsuchiya, *Heterocycles*, **22**, 1303 (1984).
11) H. Sashida and T. Tsuchiya, *Chem. Pharm. Bull.*, **32**, 4600 (1984).

12) E. L. Eliel, R. L. Willer, A. T. McPhail, and K. D. Onan, *J. Am. Chem. Soc.*, **96**, 3021 (1974); O. Hofer and E. L. Eliel, *ibid.*, **95**, 8045 (1973); E. L. Eliel and R. L. Willer, *ibid.*, **99**, 1936 (1977).
13) N. Furukawa, K. Harada, and S. Oae, *Tetrahedron Lett.*, **1972**, 1377.
14) R. W. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **18**, 563 (1979).
15) W. E. Parham and R. Koncos, *J. Am. Chem. Soc.*, **83**, 4034 (1961).
16) H. Böhme, L. Tils, and B. Unterhalt, *Chem. Ber.*, **97**, 179 (1964).