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Tetrathiomolybdate Mediated Rearrangement of Aziridinemethanol Tosylates: A Thia-Aza-Payne Rearrangement

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‡*Dedicated to Professor Henri Kagan, Universite' Paris-sud, Orsay, France on the occasion of his 80th birthday*

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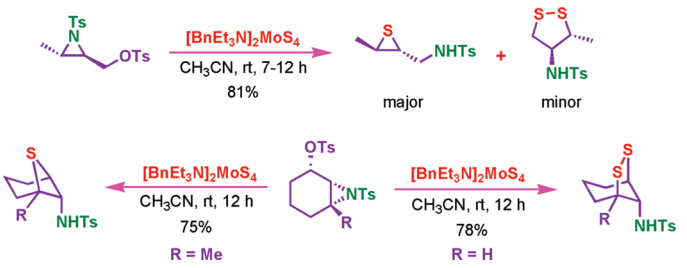

Aziridinemethanol sulfonate esters react with tetrathiomolybdate **1** to give thiirane derivatives as the major product and cyclic disulfides as minor product under mild reaction conditions via an unprecedented thia-aza-Payne-type rearrangement. Interestingly, when the reaction of **1** was carried out with 2-aziridino-cyclohexanol derivatives it resulted in the formation of thia-bicyclo[3.1.1]heptane or dithia-bicyclo[3.2.1]octane derivatives.

Introduction

Payne rearrangement of 2,3-epoxy alcohols is a well-known and widely studied reaction.[1,2] Similarly, the aza-Payne,[3] and thia-Payne[4] rearrangements of 2,3-epoxy amines and sulfides are also well studied and have received much attention.[5] The reaction of *N*-tosyl-2-aziridinemethanol tosylates and 2-epoxymethanol tosylates with selenium[6] and tellurium nucleophiles[7] in the presence of Lewis acid has been shown to provide allyl amine and allyl alcohol derivatives, respectively. One important aspect of these rearrangements is that the reaction is usually stereospecific, proceeding with inversion of configuration at the C-2 carbon of the epoxide ring via S_N2-type pathway (Scheme 1). Earlier we have reported our results on the ring-opening of aziridines using benzyltriethylammonium tetrathiomolybdate, $[BnEt_3N]_2MoS_4$ (**1**), as a sulfur transfer reagent[8] to synthesize β-aminosulfides, disulfides,[9a] functionalized unsymmetrical disulfides,[9b] and sulfur heterocycles.[10] We have also reported recently a Selena-aza-Payne-type rearrangement of aziridinemethanol tosylates using tetraethylammonium tetraselenotungstate.[11]

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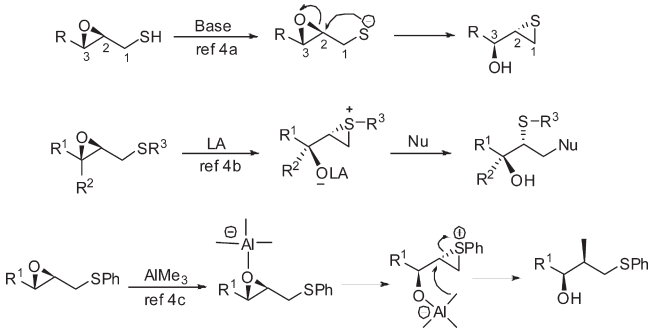
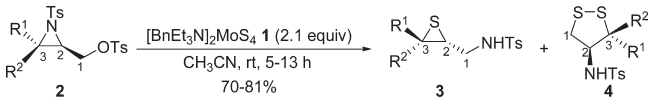
SCHEME 1. Different Types of Thia-Payne Rearrangement



SCHEME 2. Thia-Aza-Payne-Type Rearrangement of Different Aziridinemethanol Tosylates



In the present article we wish to report a detailed study on the regio- and stereospecific ring-opening of a number of aziridinemethanol tosylates **2** with **1** to afford the corresponding thiirane derivatives **3** as the major products and the cyclic-disulfides **4** as the minor products as shown in Scheme 2.

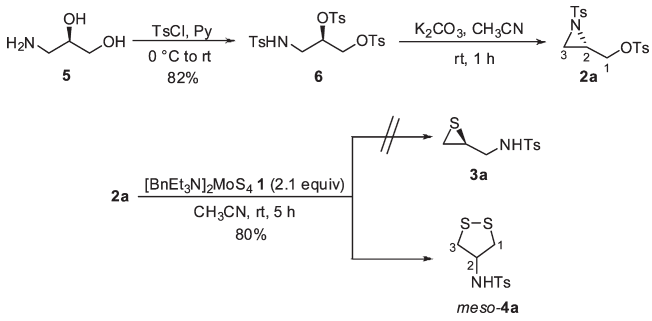
Results and Discussion

Ring-Opening of Mono- and 2,2-Disubstituted *N*-Tosyl Aziridines with 1. Our investigation began with the study of nucleophilic ring-opening of optically pure *N*-tosyl-aziridinemethanol tosylate **2a** with **1** to obtain the corresponding optically active thiirane derivative **3a**. The aziridinemethanol tosylate **2a** was synthesized in 90% yield from (*R*)-3-amino-1,2-propanediol (**5**), by tosylation with *p*-toluenesulfonyl chloride in pyridine followed by cyclization of **6** with potassium carbonate.[12] Treatment of **2a** with **1** [2.1 equiv, CH_3CN, 28 °C, 8 h] failed to furnish the thiirane derivative **3a**, but resulted in a smooth ring-opening at C3 in a regiospecific manner followed by cyclization to afford *meso*-cyclic disulfide derivative **4a** as the single product in 80% yield (Scheme 3).

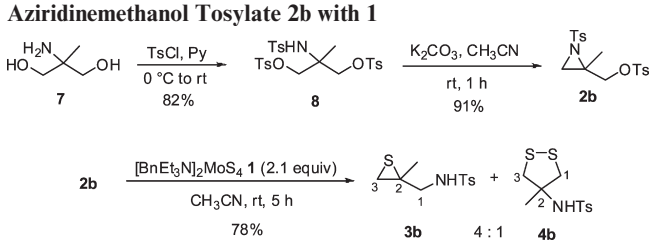
This methodology was then extended to the reaction of 2,2-disubstituted aziridinemethanol tosylate **2b**. Compound **2b** was synthesized from 2-amino-2-methyl-1,3-propanediol (**7**) via the ditosylate **8** as shown in Scheme 4.[11] Treatment of **2b** with **1** [2.1 equiv, CH_3CN, 28 °C, 8 h] furnished the desired thiirane derivative **3b** as the major product and cyclic disulfide derivative **4b** as the minor product (4:1 ratio) in 78% yield. In the course of this thia-aza-Payne-type rearrangement to form **3b**, nitrogen migration occurs from C3, C2 to C1 position (Scheme 4).

General Synthesis of Other Aziridinemethanol Tosylates. To expand the scope of this methodology, synthesis of a number of aziridinemethanol tosylates **2** was achieved starting from allylic alcohols **9** using Sharpless's aziridination protocol[13] [allylic alcohol, 3 mmol; CAT (Chloramine-T), 3.3 mmol; PTAB (phenyltrimethylammonium tribromide),

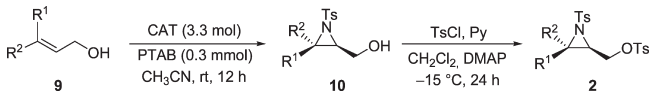
SCHEME 3. Regiospecific Ring-Opening of Aziridine Methanol Tosylate 2a with 1



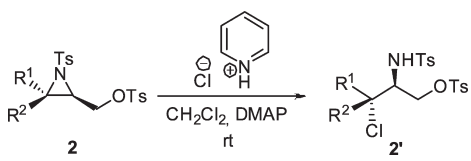
SCHEME 4. Regiospecific Ring-Opening of Disubstituted Aziridinemethanol Tosylate 2b with 1



SCHEME 5. Synthesis of Aziridinemethanol Tosylates 2 from Allylic Alcohols 9



SCHEME 6. Ring-Opening of Aziridinemethanol Tosylates 2 with Chloride Ion (Cl^-)



0.3 mmol; 15 mL of CH_3CN, rt, 12 h] followed by tosylation of aziridinemethanols **10** with *p*-toluenesulfonyl chloride, a catalytic amount of DMAP, and pyridine in CH_2Cl_2 at −15 °C for 24 h (Scheme 5).

When performing the tosylation of aziridinemethanols **10**, care has to be taken while doing the workup; before quenching the excess pyridine and DMAP with dilute HCl, the reaction mixture has to be diluted with diethyl ether at −15 °C. Otherwise, the aziridine tosylate **2** undergoes ring-opening with chloride ion (Cl^-) of pyridinium hydrochloride to give ring-opened product **2′** as shown in Scheme 6.

Ring-Opening of 2,3-Disubstituted *N*-Tosyl Aziridines with 1. To address the issue of whether the reaction of **1** takes place at the tosylate first or aziridine ring opens first and assess the regio- and stereospecificity of aziridine ring-opening, this methodology was then extended to the reaction of (±)-*trans*-*N*-tosyl aziridinemethanol tosylate **2c** with **1** (2.1 equiv; CH_3CN, 28 °C, 6 h). This led to the formation of *trans*-thiirane derivative **3c** as the major product and *trans*-cyclic disulfide derivative **4c** as the minor product

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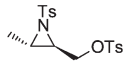
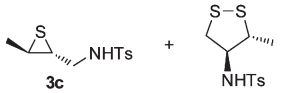
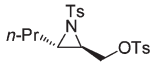
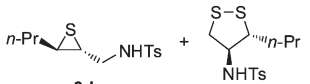
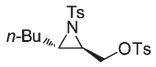
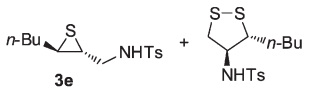
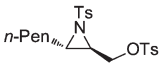
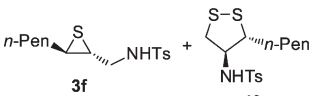
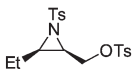
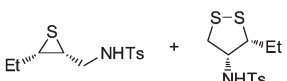
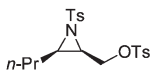
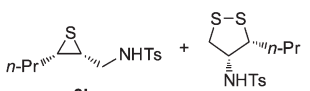
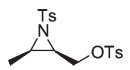
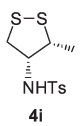
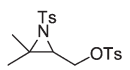
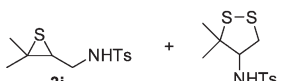
TABLE 1. Thia-Aza-Payne-Type Rearrangement of Different Aziridinemethanol Tosylates 2d−j

Entry	Aziridine tosylate	Product	Ratio	Time (h)	Yield (%)
1	 **2c**	 **3c** + **4c**	3 : 1	6	81
2	 **2d**	 **3d** + **4d**	4 : 1	10	78
3	 **2e**	 **3e** + **4e**	4 : 1	11	76
4	 **2f**	 **3f** + **4f**	4 : 1	12	72
5	 **2g**	 **3g** + **4g**	4 : 1	12	65
6	 **2h**	 **3h** + **4h**	4 : 1	12	64
7	 **2i**	 **4i**	-	7	60
8	 **2j**	 **3j** + **4j** and	3 : 1	8	80

(3:1) in good yield with excellent regio- and stereocontrol (Table 1, entry 1). The stereochemistry of compounds **3c**[14] and **4c**[15] was confirmed by single-crystal X-ray analysis (see the Supporting Information).

Subsequently, the reaction of **1** with a number of *trans*-2,3-disubstituted aziridinemethanol tosylates **2d−f** was studied and in all the cases the reaction proceeded smoothly to give the corresponding *trans*-thiirane derivatives **3d−f** as the major products and the cyclic disulfides **4d−f** as the minor products with excellent regio- and stereocontrol (Table 1, entries 2−4).

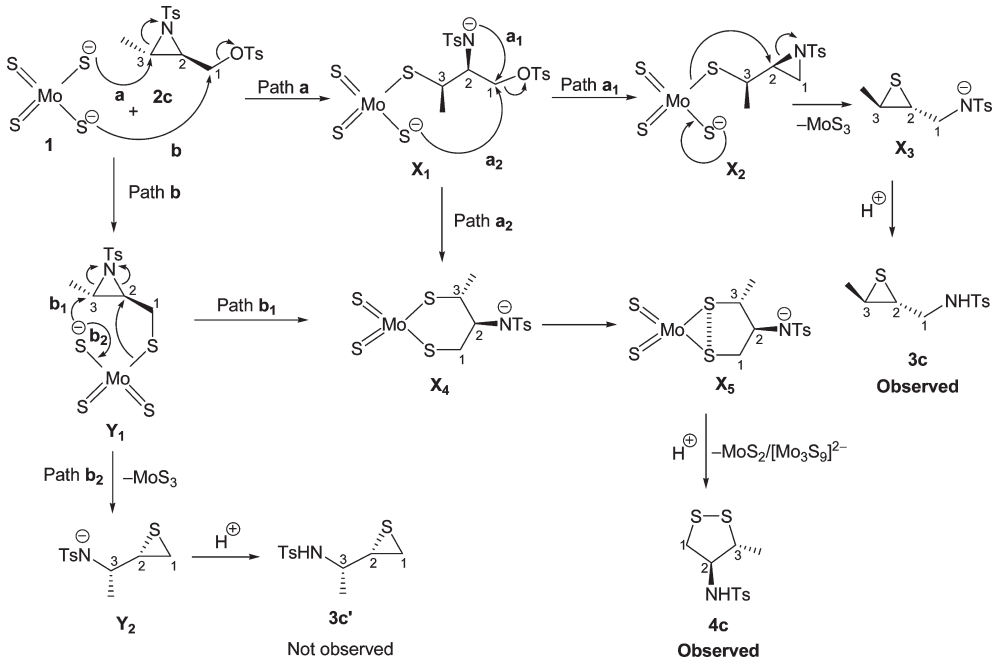
The reaction of (±)-*cis*-*N*-tosyl aziridinemethanol tosylate **2g** with **1** [2.1 equiv; CH_3CN, 28 °C, 12 h] led to the formation of the *cis*-thiirane **3g** as the major product and *cis*-cyclic disulfide **4g** as the minor product (4:1) in good yield. Similarly, **2h** on treatment with **1** gave **3h** and **4h** in 4:1 ratio as shown in Table 1, entries 5 and 6. Interestingly, aziridinemethanol tosylate **2i** failed to undergo the rearrangement, but gave the cyclic disulfide **4i** as the only product in 60% yield (entry 7).[16]

(14) The structure was solved by direct methods (SIR92). Refinement was by full-matrix least-squares procedures on F^2 by using SHELXL-97. CCDC No. 288573. Crystal system: monoclinic; space group: $P2_1/n$; cell parameters: a = 5.169(3) Å, b = 29.506(1) Å, c = 8.521(5) Å, a = 90.00°, b = 100.04(1)°, g = 90.00°, V = 1279(3) Å^3, Z = 4, ρ_{calcd} = 1.34 g cm^{-3}, $F(000)$ = 543.9, m = 0.40 mm^{-1}, l = 0.71073 Å. Total number l.s. parameters = 145. R_1 = 0.057 for 2240 $F_o > 4\sigma(F_o)$ and 0.09 for all 9066 data. wR_2 = 0.153, GOF = 1.000, restrained GOF = 1.000 for all data.

(15) The structure was solved by direct methods (SIR92). Refinement was by full-matrix least-squares procedures on F^2 by using SHELXL-97. CCDC No. 288574. Crystal system: monoclinic; space group: $P2_1/n$; cell parameters: a = 12.469(7) Å, b = 7.347(4) Å, c = 15.965(9) Å, a = 90.00°, b = 112.404(9)°, g = 90.00°, V = 1352.3(6) Å^3, Z = 4, ρ_{calcd} = 1.42 g cm^{-3}, $F(000)$ = 607.9, m = 0.54 mm^{-1}, l = 0.71073 Å. Total number l.s. parameters = 154. R_1 = 0.056 for 2370 $F_o > 4\sigma(F_o)$ and 0.067 for all 9165 data. wR_2 = 0.146, GOF = 1.138, restrained GOF = 1.138 for all data.

(16) In the case of **2i** the formation of only *cis*-cyclic disulfide derivative **4i** during the reaction remains to be studied further.

SCHEME 7. Tentative Mechanism for the Formation of 3c and 4c



The reaction of 2,3,3-trisubstituted aziridinemethanol tosylate **2j** with **1** (2.1 equiv, CH_3CN, 28 °C, 13 h) furnished thiirane derivative **3j** as the major product and the cyclic disulfide **4j** (3:1) as the minor product in good yields (Table 1, entry 8). The structure of cyclic disulfide **4j**[17] was confirmed by single-crystal X-ray analysis (Figure 1).

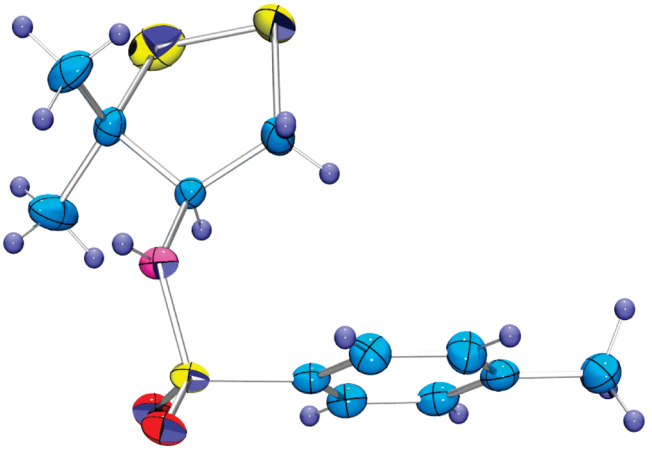


FIGURE 1. X-ray ORTEP diagram of compound **4j**.

Tentative Mechanism for the Thia-Aza-Payne-Type Rearrangement. On the basis of the results of this investigation, a tentative mechanism for the formation of products **3c** and **4c** is presented in Scheme 7 and it is analogous to the pathway suggested earlier in the case of tetraselenotungstate.[11] In the course of this thia-aza-Payne-type rearrangement to from **3c**, nitrogen migration occurs from C2, C3 to C1 position, with the formation of thiirane **3c** with same stereochemistry. During the formation of **3c**, the reaction tends to follow path a. In path a, tetrathiomolybdate **1** attacks the aziridine **2c** at C3 in an S_N2 fashion to give intermediate $\mathbf{X_1}$, which can further go through two different pathways: path a_1 and a_2. In path a_1, intramolecular displacement of the tosyl group by nitrogen nucleophile would give an aziridine intermediate $\mathbf{X_2}$. Ring-opening of the newly formed aziridine $\mathbf{X_2}$ by sulfur nucleophile will give the thiirane intermediate $\mathbf{X_3}$, which after protonation leads to thiirane derivative **3c** with trans stereochemistry. In path a_2, intramolecular displacement of tosylate by sulfur nucleophile would give a six-membered intermediate $\mathbf{X_4}$. This intermediate can lead to cyclic disulfide **4c** (observed experimentally) by an internal redox process[18] with elimination of $MoS_2/[Mo_3S_9]^{2-}$ as byproducts.

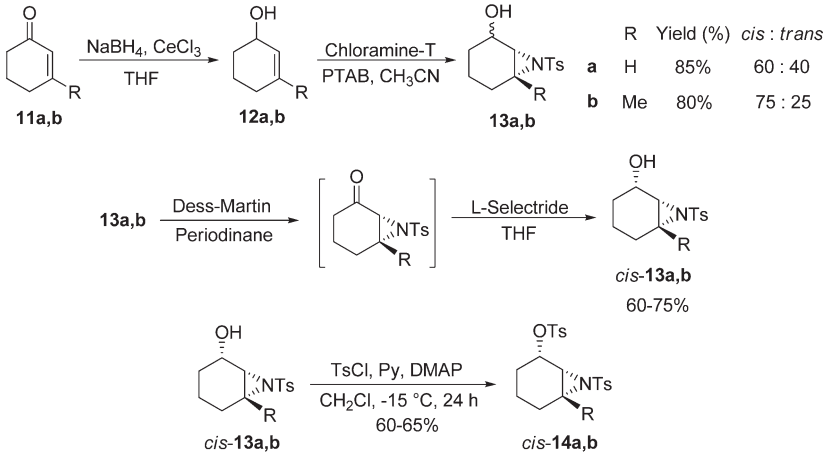
In path b, tetrathiomolybdate **1** attacks the aziridine **2c** at the C1 position in an S_N2 fashion to give intermediate $\mathbf{Y_1}$, which can further undergo two types of reactions via either path b_1 or b_2. In path b_1, nucleophilic ring-opening of aziridine at C3 with sulfur nucleophile would give six-membered intermediate $\mathbf{X_4}$, which undergoes further transformation to give cyclic disulfide **4c** as mentioned in the case of path a_2. In path b_2, sulfur nucleophile attacks the aziridine at C2 to give thiirane intermediate $\mathbf{Y_2}$, which undergoes further protonation during workup to give 1,2-thiirane derivative **3c′** (not observed experimentally). On the basis of these observations one may conclude that in the reaction of **2c** with **1** the ring-opening of aziridine takes place first followed by further reaction with the tosylate to give the observed products.

Reaction of Tetrathiomolybdate 1 with Aziridino-Tosylates Derived from Cyclic-Allylic Alcohols. Finally, this methodol-

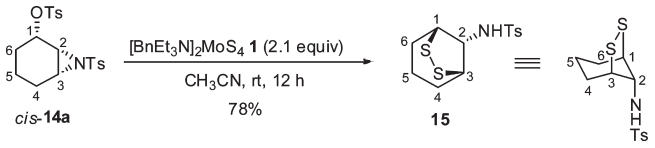
(17) The structure was solved by direct methods (SIR92). Refinement was by full-matrix least-squares procedures on F^2 by using SHELXL-97. CCDC No. 648189. Crystal system: triclinic; space group: $P\bar{1}$; cell parameters: a = 7.238(4) Å, b = 10.304(5) Å, c = 10.950(6) Å, a = 109.161(8)°, b = 102.369(8)°, g = 94.459(9)°, V = 743.8(3) Å^3, Z = 2, ρ_{calcd} = 1.35 g cm^{-3}, $F(000)$ = 320, m = 0.49 mm^{-1}, l = 0.71073 Å. Total number l.s. parameters = 232. R_1 = 0.047 for 2615 $F_o > 4\sigma(F_o)$ and 0.052 for all 7163 data. wR_2 = 0.139, GOF = 1.036, restrained GOF = 1.036 for all data.

(18) (a) Kruhlak, N. L.; Wang, M.; Boorman, P. M.; Parvez, M.; McDonald, R. *Inorg. Chem.* **2001**, *40*, 3141–3148. (b) Boorman, P. M.; Wang, M.; Parvez, M. *J. Chem. Soc., Chem. Commun.* **1995**, 999–1000.

SCHEME 8. Synthesis of *cis*-*N*-Tosyl Aziridine Tosylate Derivatives 14a,b



SCHEME 9. Reaction of *cis*-*N*-Tosyl Aziridine Tosylate Derivative 14a with 1



ogy was extended to the reaction of *cis*-aziridino tosylates **14a** and **14b** with **1**. The *cis*-*N*-tosyl aziridino-alcohols **13a**,**b** were synthesized by using the literature procedure reported by O'Brien et al.[19] This procedure starts with cyclohexenol derivatives **12a**,**b**, prepared by Luche[20] reduction of the cyclohexenones **11a**,**b**. Aziridination of **12a**,**b** with the Sharpless aziridination protocol[13] [cyclo-hexenol, 3 mmol; CAT, 3.3 mmol; PTAB, 0.3 mmol; 15 mL of CH_3CN, rt, 16 h] gave hydroxy aziridines **13a**,**b** in high yields (80−85%) and with a satisfactory degree of cis selectivity (Scheme 8).

The *cis*- and *trans*-aziridines **13a**,**b** can be separated by chromatography to give 44−65% isolated yields of *cis*-**13a**,**b**. Alternatively, an oxidation−reduction sequence (via the keto aziridines[21]) can be utilized to produce single diastereomers of *cis*-hydroxy aziridines **13a**,**b**. Reduction of the keto aziridines with L-selectride in THF at −78 °C furnished *cis*-aziridino alcohols **13a**,**b** in good yields with high stereoselectivity.[22] Further, tosylation of *cis*-**13a**,**b** with *p*-toluenesulfonyl chloride, triethylamine, pyridine, and DMAP in CH_2Cl_2 at −15 °C for 24 h furnished the corresponding *cis*-*N*-tosyl aziridine tosylates **14a**,**b** in 60−65% yields (Scheme 8).

With the pure compounds in hand, the *cis*-*N*-tosyl aziridine tosylate **14a** was treated with **1** [2.1 equiv; CH_3CN, 28 °C, 12 h] to furnish exclusively the dithia-bicyclo[3.2.1]octane derivative **15** in 78% yield without going through the thia-aza-Payne-type rearrangement pathway (Scheme 9). The structure of compound **15** was confirmed by ^1H, ^{13}C NMR, DEPT, $^1H-^1H$, $^1H-^{13}C$ COSY, NOE, and HRMS studies. The solid state structure of **15**[23] was confirmed by single-crystal X-ray analysis (Figure 2).

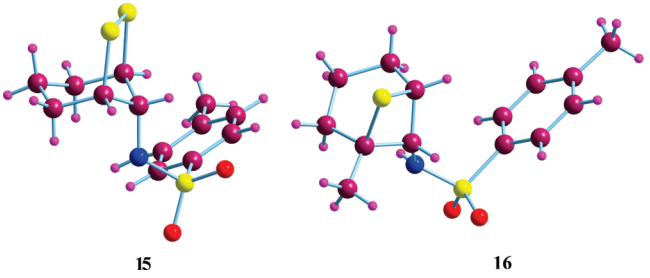


FIGURE 2. X-ray structures of compounds **15** and **16**.

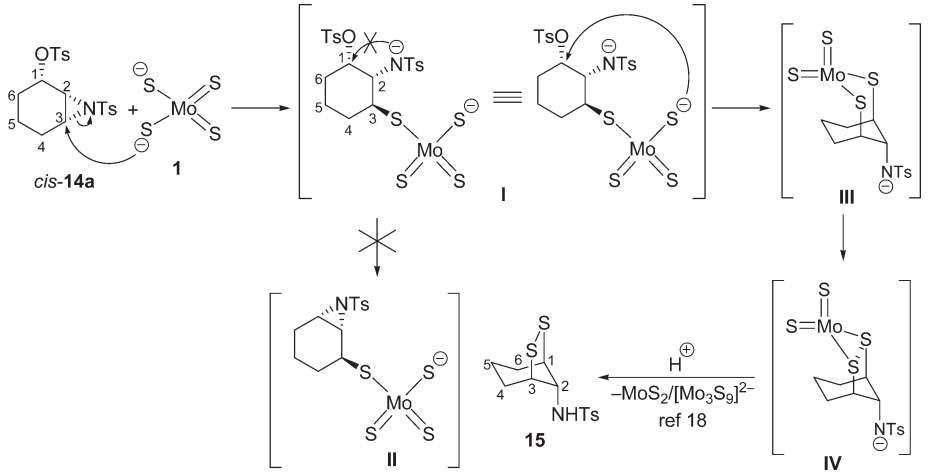
The absence of thia-aza-Payne rearrangement in the case of **14a** is certainly an expected result. The formation of aza anion and tosylate leaving group (intermediate **I**) are cis to each other, and as a result it cannot undergo intramolecular S_N2 displacement of tosylate by aza anion to give intermediate **II** (Scheme 10). Alternatively, displacement of the tosyl group by sulfur nucleophile would give a six-membered intermediate **III**. This intermediate can lead to dithia-bicyclo[3.2.1]octane derivative **15** by an internal redox process[18] with elimination of $MoS_2/[Mo_3S_9]^{2-}$ as byproducts.

When the same reaction was extended to aziridino-tosylate **14b** with **1** [2.1 equiv; CH_3CN, 28 °C, 12 h] an unusual thia-bicyclo[3.1.1]heptane derivative **16** was obtained as the exclusive product in 75% yield (Scheme 11). The regio- and stereochemical outcome of the reaction was confirmed by solving the solid state structure of compound **16**[24] by X-ray crystallographic analysis (Figure 2).

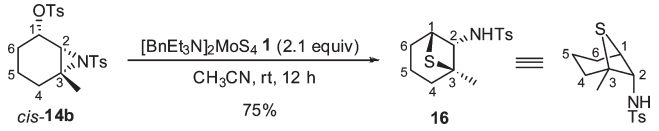
The formation of **16** can be explained as shown in Scheme 12. First, the *cis*-aziridine **14b** undergoes ring-opening with **1**

(19) Rosser, C. M.; Coote, S. C.; Kirby, J. P.; O' Brien, P.; Caine, D. *Org. Lett*. **2004**, *6*, 4817–4819.
(20) Luche, J.-L. F. *J. Am. Chem. Soc*. **1978**, *100*, 2226–2227.
(21) (a) Fioravanti, S.; Pellacani, L.; Tabanella, S.; Tardella, P. A. *Tetrahedron* **2003**, *54*, 14105–14112. (b) Barros, M. T.; Maycock, C. D.; Ventura, M. R. *Tetrahedron Lett*. **2002**, *43*, 4329–4331.
(22) Dechoux, L.; Doris, E.; Mioskowski, C. *Chem. Commun*. **1996**, 549−550 and references cited therein.
(23) The structure was solved by direct methods (SIR92). Refinement was by full-matrix least-squares procedures on F^2 by using SHELXL-97. CCDC No. 648187. Crystal system: monoclinic; space group: $P2_1/c$; cell parameters: a = 12.005(8) Å, b = 25.176(3) Å, c = 10.735(7) Å, a = 90.00°, b = 113.31(4)°, g = 90.00°, V = 2979.6(13) Å^3, Z = 8, ρ_{calcd} = 1.41 g cm^{-3}, $F(000)$ = 1327.9, m = 0.49 mm^{-1}, l = 0.71073 Å. Total number l.s. parameters = 351. R_1 = 0.057 for 6008 $F_o > 4\sigma(F_o)$ and 0.073 for all 22253 data. wR_2 = 0.136, GOF = 1.085, restrained GOF = 1.085 for all data.

SCHEME 10. Suggested Mechanism for the Formation of Thia-Bicyclo[3.2.1]octane Derivative 15



SCHEME 11. Reaction of *cis*-*N*-Tosyl Aziridine Tosylate Derivative 14b with 1

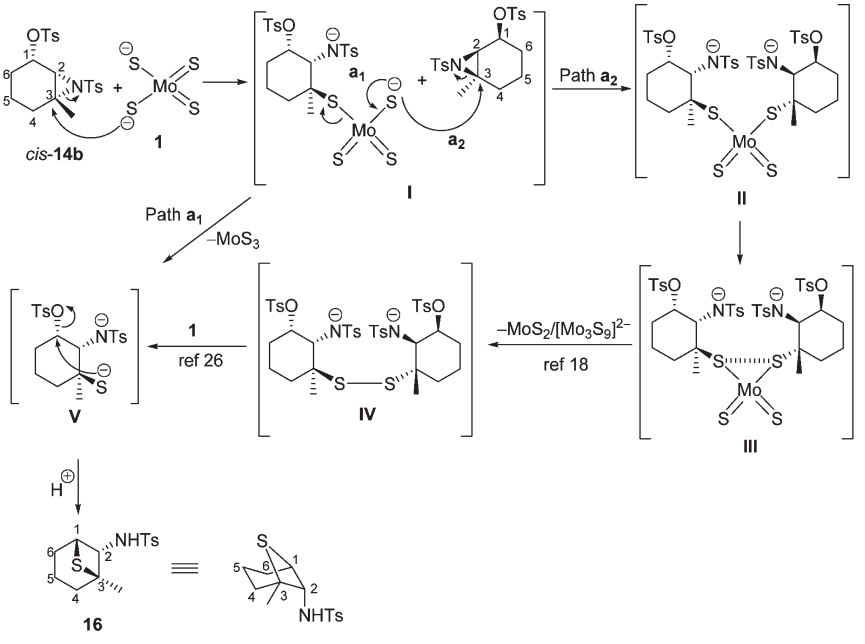


at the more substituted carbon in an S_N2 fashion[25] to give intermediate **I**, which can further go through two different pathways: path a_1 and a_2. In path a_1, it is possible to visualize the elimination of MoS_3 from intermediate **I** followed by intramolecular displacement of tosylate by the thiolate intermediate **V** to give the product. In path a_2, the intermediate **I** attacks another aziridine **14b** in a similar manner to give the bisalkylated intermediate **II**. The intermediate **II** is readily poised for S−S bond formation by internal redox process[18] with the elimination of $MoS_2/[Mo_3S_9]^{2-}$ to give disulfide intermediate **IV**. In the presence of excess tetrathiomolybdate **1**, the intermediate **IV** undergoes in situ reductive cleavage of the disulfide bond[26] to give the thiolate intermediate **V**. Both pathways lead to the same thiolate intermediate **V**, which can then give the thia-bicyclo[3.1.1]heptane derivative **16** as shown in Scheme 12.

Conclusion

In conclusion, we have shown that *N*-tosyl aziridinemethanol tosylates undergo a new type of thia-aza-Payne-type rearrangement with tetrathiomolybdate **1** to give the corresponding thiirane derivatives as the major products and five-membered cyclic disulfides as the minor products with good regio- and stereocontrol. However, *cis*-*N*-tosyl aziridine tosylates **14a**,**b** failed to undergo thia-aza-Payne-type rearrangement with tetrathiomolybdate **1** but led to the formation of bicyclo[3.2.1]octane derivative **15** and thia-bicyclo[3.1.1]heptane derivative **16**, respectively, as exclusive product.

SCHEME 12. Suggested Mechanism for the Formation of Thia-Bicyclo[3.1.1]heptane Derivative 16



Experimental Section

Compounds **2a**,[12] **10**,[13] **13a**, and **13b**[19] were synthesized according to literature procedure.

Synthesis of Compound 2b. To a stirred solution of 2-amino-2-methyl-1,3-propanediol **7** (1.00 g, 9.52 mmol) in dry pyridine (20 mL) maintained at ice temperature was added a solution of *p*-toluenesulfonyl chloride (5.43 g, 28.56 mmol) in pyridine (10 mL) over a 2 h period. The resulting yellow suspension was refrigerated overnight, acidified with ice-cold 6 N HC1, and then extracted with methylene chloride (3 × 20 mL). The combined extracts were washed with 5% aqueous $NaHCO_3$, (2 × 10 mL), dried over $MgSO_4$, and concentrated in vacuo to give a syrupy residue. Silica gel chromatography (chloroform−methanol, 95:5) of this residue afforded ditosylate **8** (4.43 g, 82%) as a colorless syrup. This syrup was dissolved in acetonitrile (30 mL) and K_2CO_3 (2.16 g, 15.63 mmol) was added and stirred for 1 h at room temperature. The solvent was removed under reduced pressure and the residue was partitioned between water (20 mL) and methylene chloride (20 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated under vacuum to give a syrupy residue. Silica gel chromatography (ethylacetate−hexanes, 9:1) of this residue afforded **2b**[27] as a colorless solid. R_f 0.60 (EtOAc/hexanes, 3:7); yield 2.81 g, 91%; mp 90 °C; IR (neat) ν_{max} 1596, 1367, 1321, 1161, 972, 832, 670 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, J = 8.1 Hz, 4H), 7.35 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H), 4.03 (d, J = 10.5 Hz, 1H), 3.93 (d, J = 10.5 Hz, 1H), 2.61 (s, 1H), 2.46 (s, 3H), 2.44 (s, 3H), 2.37 (s, 1H), 1.67 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.2, 144.4, 136.9, 132.5, 129.9, 129.6, 127.9, 127.5, 72.9, 46.6, 39.0, 21.7, 21.6, 15.9; HR-MS m/z calcd for $C_{18}H_{21}NO_5S_2$ [M + Na^+] 418.0759, found 418.0766.

General Procedure for the Synthesis of *N*-Tosyl Aziridinemethanol Tosylates. To a solution of appropriate aziridinoalcohols **10**[13] (0.68 mmol) in CH_2Cl_2 (2 mL) cooled to −15 °C was added pyridine (0.17 mL, 2.1 mmol), DMAP (10 mg, 0.08 mmol), and *p*-toluenesulfonyl chloride (0.270 g, 1.4 mmol). After stirring for 24 h at −15 °C, the solution was diluted with ether at −15 °C (50 mL) and washed with water, 1 M HCl, saturated $NaHCO_3$, and water. The organic phase was dried over $MgSO_4$ and concentrated in vacuo and the crude product was purified by flash column chromatography (230−400 mesh, eluting with 20% EtOAc/hexanes) to give the corresponding *N*-tosyl aziridinemethanol tosylates **2** in good yields.

Compound 2c: R_f 0.65 (EtOAc/hexanes, 3:7); colorless syrup; yield 0.210 g, 78%; IR (neat) ν_{max} 1597, 1495, 1453, 1361, 1324, 1177, 1092, 970, 815, 709, 685, 664 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 4H), 4.17 (dd, J = 11.0, 5.7 Hz, 1H), 3.96 (dd, J = 11.0, 6.3 Hz, 1H), 2.98−3.03 (m, 1H), 2.73−2.79 (m, 1H), 2.44 (s, 6H), 1.56 (d, J = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.1, 144.3, 137.0, 132.4, 129.8, 129.5, 127.8, 127.4, 68.4, 45.0, 43.6, 21.7, 21.6, 14.1; HR-MS m/z calcd for $C_{18}H_{21}NO_5S_2$ [M^+ + Na] 418.0759, found 418.0768.

Compound 2d: R_f 0.70 (EtOAc/hexanes, 3: 7); colorless syrup; yield 0.218 g, 76%; IR (neat) ν_{max} 1597, 1365, 1323, 1160, 966, 814, 693 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, J = 8.1 Hz, 2H), 7.68 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 4.26 (dd, J = 11.4, 6.3 Hz, 1H), 4.14 (dd, J = 11.4, 6.0 Hz, 1H), 2.98−2.93 (m, 1H), 2.73−2.67 (m, 1H), 2.44 (s, 3H), 2.43 (s, 3H), 1.85−1.63 (m, 2H), 1.46−1.23 (m, 2H), 0.89 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.1, 144.3, 136.7, 132.4, 129.9, 129.5, 127.9, 127.5, 68.0, 47.5, 44.9, 30.9, 21.6, 21.5, 20.6, 13.5; HR-MS m/z calcd for $C_{20}H_{25}NO_5S_2$ [M^+ + Na] 446.1072, found 446.1086.

Compound 2e: R_f 0.70 (EtOAc/hexanes, 3:7); yield 0.213 g, 72%; IR (neat) ν_{max} 1597, 1364, 1324, 1160, 1094, 965, 814, 693, 667 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 4.27 (dd, J = 10.8, 5.7 Hz, 1H), 4.14 (dd, J = 10.8, 6.3 Hz, 1H), 2.98−2.93 (m, 1H), 2.71−2.66 (m, 1H), 2.45 (s, 3H), 2.44 (s, 3H), 1.77−1.70 (m, 2H), 1.29−1.27 (m, 4H), 0.85 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.1, 144.3, 136.7, 132.4, 129.9, 129.5, 127.9, 127.5, 127.4, 68.0, 47.7, 44.9, 29.4, 28.8, 22.0, 21.6, 21.5, 13.8; HR-MS m/z calcd for $C_{21}H_{27}NO_5S_2$ [M^+ + Na] 460.1228, found 460.1239.

Compound 2f: R_f 0.70 (EtOAc/hexanes, 3:7); yield 0.184 g, 60%; IR (neat) ν_{max} 1597, 1365, 1325, 1160, 1095, 969, 814, 693, 666 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 4.27 (dd, J = 10.8, 5.7 Hz, 1H), 4.15 (dd, J = 10.8, 6.3 Hz, 1H), 2.96 (dd, J = 10.2, 5.7 Hz, 1H), 2.69 (dd, J = 10.2, 6.6 Hz, 1H), 2.44 (s, 3H), 2.43 (s, 3H), 1.74−1.69 (m, 1H), 1.28−1.24 (m, 7H), 0.85 (t, J = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.1, 144.3, 136.7, 132.4, 129.9, 129.5, 127.8, 127.5, 127.5, 67.9, 47.7, 44.9, 31.0, 29.0, 26.9, 22.3, 21.6, 21.5, 13.8; HR-MS m/z calcd for $C_{22}H_{29}NO_5S_2$ [M^+ + Na] 474.1385, found 474.1385.

Compound 2g: R_f 0.70 (EtOAc/hexanes, 3:7); yield 0.178 g, 64%; IR (neat) ν_{max} 1596, 1368, 1335, 1160, 962, 834, 678 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, J = 8.1 Hz, 2H), 7.69 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 4.07 (dd, J = 6.6, 1.0 Hz, 1H), 3.06 (dd, J = 13.5, 6.6 Hz, 1H), 2.83−2.76 (m, 1H), 2.45 (s, 3H), 2.44 (s, 3H), 1.56−1.42 (m, 1H), 1.38−1.23 (m, 1H), 0.86 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.2, 144.8, 134.3, 132.3, 129.9, 129.6, 128.0, 127.9, 66.1, 45.2, 40.9, 21.6, 20.2, 11.5; HR-MS m/z calcd for $C_{19}H_{23}NO_5S_2Na^+$ [M + Na^+] 432.0915, found 432.0922.

Compound 2h: R_f 0.70 (EtOAc/hexanes, 3:7); colorless syrup; yield 0.186 g, 65%; IR (neat) ν_{max} 1597, 1366, 1328, 1161, 1092, 975, 815, 720, 667 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, J = 8.1 Hz, 2H), 7.69 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1 Hz, 4H), 3.99 (d, J = 6.6 Hz, 2H), 3.04 (dd, J = 13.8, 6.6 Hz, 1H), 2.86 (dd, J = 13.8, 7.5 Hz, 1H), 2.45 (s, 6H), 1.44−1.17 (m, 4H), 0.84 (t, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.2, 144.8, 134.3, 132.2, 129.9, 129.6, 127.9, 127.8, 66.1, 43.6, 40.8, 28.6, 21.6, 20.4, 13.5; HR-MS m/z calcd for $C_{20}H_{25}NO_5S_2$ [M^+ + Na] 446.1072, found 446.1081.

Compound 2i: R_f 0. 70 (EtOAc/hexanes, 3:7); colorless syrup; yield 0.188 g, 70%; IR (neat) ν_{max} 1592, 1371, 1331, 1168, 966, 835, 671 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, J = 8.1 Hz, 2H), 7.68 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1 Hz, 4H), 3.99 (d, J = 6.3 Hz, 2H), 3.03−2.92 (m, 2H), 2.45 (s, 6H), 1.17 (d, J = 5.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.2, 144.8, 134.5, 132.3, 129.9, 129.7, 127.8, 65.9, 40.7, 38.9, 21.6, 11.9; HR-MS m/z calcd for $C_{18}H_{21}NO_5S_2$ [M^+ + Na] 418.0759, found 418.0759.

Compound 2j: R_f 0.60 (EtOAc/hexanes, 3:7); yield 0.183 g, 66%; IR (neat) ν_{max} 1595, 1366, 1326, 965, 816, 682, 665 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, J = 8.1 Hz, 2H), 7.64 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 8.1 Hz,

(24) The structure was solved by direct methods (SIR92). Refinement was by full-matrix least-squares procedures on F^2 by using SHELXL-97. CCDC No. 648188. Crystal system: triclinic, space group: $P\bar{1}$; cell parameters: a = 7.530(2) Å, b = 8.964(2) Å, c = 11.913(3) Å, a = 77.985(4)°, b = 75.57(4)°, g = 88.780(4)°, V = 761.3(1) $Å^3$, Z = 2, ρ_{calcd} = 1.30 g cm^{-3}, $F(000)$ = 316, m = 0.35 mm^{-1}, l = 0.71073 Å. Total number l.s. parameters = 178. R_1 = 0.084 for 258 $F_o > 4\sigma(F_o)$ and 0.103 for all 6646 data. wR_2 = 0.225, GOF = 1.030, restrained GOF = 1.030 for all data.

(25) (a) Forbeck, E. M.; Evans, C. D.; Gilleran, J. A.; Li, P.; Joullié, M. M. *J. Am. Chem. Soc.* **2007**, *129*, 14463–14469. (b) Li, P.; Forbeck, E. M.; Evans, C. D.; Joullié, M. M. *Org. Lett.* **2006**, *8*, 5105–5107. (c) Lin, P.; Bellos, K.; Stamm, H.; Onistschenko, A. *Tetrahedron* **1992**, *48*, 2359–2372.

(26) (a) Pan, W. H.; Harmer, M. A.; Halbert, T. R.; Stiefel, E. I. *J. Am. Chem. Soc.* **1984**, *106*, 459–460. (b) Coyle, C. L.; Harmer, M. A.; George, G. N.; Daage, M.; Stiefel, E. I. *Inorg. Chem.* **1990**, *29*, 14−19 and references cited therein. (c) Prabhu, K. R.; Sivanand, P.; Chandrasekaran, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 4316–4319.

(27) Chao, B.; Dittmer, D. C. *Tetrahedron Lett.* **2001**, *42*, 5789–5791.

2H), 4.02 (dd, J = 10.8, 5.7 Hz, 1H), 3.86 (dd, J = 10.8, 6.6 Hz, 1H), 3.13 (t, J = 6.6 Hz, 1H), 2.45 (s, 3H), 2.43 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.1, 144.0, 137.5, 132.3, 129.9, 129.5, 127.8, 127.3, 67.3, 51.2, 48.1, 21.6, 21.5, 21.2, 20.8; HR-MS m/z calcd for $C_{19}H_{23}NO_5S_2$ [M^+ + Na] 432.0915, found 432.0927.

General Procedure for the Synthesis of *cis*-*N*-Tosyl Aziridinemethanol Tosylates 14. To a solution of appropriate *cis*-aziridino-alcohols **13**[19] (0.68 mmol) in CH_2Cl_2 (2 mL) cooled to −15 °C was added pyridine (0.17 mL, 2.1 mmol), DMAP (10 mg, 0.08 mmol), and *p*-toluenesulfonyl chloride (0.270 g, 1.4 mmol). After being stirred for 24 h at −15 °C, the solution was diluted with ether at −15 °C (50 mL) and washed with water, 1 M HCl, saturated $NaHCO_3$, and water. The organic phase was dried over $MgSO_4$ and concentrated in vacuo. Purification by flash column chromatography on silica gel (20% EtOAc/hexanes) gave the corresponding *cis*-aziridino-tosylates **14** as a colorless syrup in good yields.

Compound 14a: R_f 0.40 (EtOAc/hexanes, 3:7); yield 0.186 g, 65%; IR (neat) ν_{max} 1597, 1365, 1327, 1189, 1176, 1161, 1093, 989, 814, 726, 670 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, J = 8.1 Hz, 2H), 7.64 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 4.70−4.64 (m, 1H), 3.19 (t, J = 6.6 Hz, 1H), 3.01 (dd, J = 7.2, 3.3 Hz, 1H), 2.44 (s, 6H), 1.91−1.66 (m, 2H), 1.59−1.53 (s, 3H), 1.31−1.10 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.7, 144.5, 134.5, 133.6, 129.7, 129.5, 127.9, 127.6, 75.8, 41.6, 40.7, 25.4, 21.6, 21.5, 20.8, 19.9; HR-MS m/z calcd for $C_{20}H_{23}NO_5S_2$ [M^+ + Na] 444.0915, found 444.0920.

Compound 14b: R_f 0.50 (EtOAc/hexanes, 3:7); yield 0.177 g, 60%; IR (neat) ν_{max} 1597, 1321, 1188, 1175, 1157, 1090, 940, 873, 814, 736, 666 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (d, J = 8.1 Hz, 2H), 7.81 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 7.24 (d, J = 8.1 Hz, 2H), 4.76−4.70 (m, 1H), 3.23 (d, J = 3.9 Hz, 1H), 2.44 (s, 6H), 2.40 (s, 3H), 2.00−1.83 (m, 1H), 1.67 (s, 3H), 1.62−1.28 (m, 4H), 1.27−1.16 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.6, 143.6, 137.6, 133.8, 129.7, 129.2, 127.5, 127.4, 76.1, 53.1, 48.7, 29.9, 25.4, 21.6, 21.5, 20.6, 18.9; HR-MS m/z calcd for $C_{21}H_{25}NO_5S_2$ [M^+ + Na] 458.1072, found 458.1083.

General Procedure for the Reaction of *N*-Tosyl Aziridinemethanol Tosylates with Benzyltriethylammonium Tetrathiomolybdate 1. To a well-stirred solution of the appropriate *N*-tosyl aziridino-tosylate **2** (0.50 mmol) in CH_3CN (8 mL) was added tetrathiomolybdate **1** (0.639 g, 1.05 mmol) at once with stirring at room temperature (28 °C) until the disappearance of starting material (TLC, 5−13 h). The solvent was evaporated under reduced pressure and the black residue was extracted with CH_2Cl_2:Et_2O (1:5, 3 × 10 mL) and filtered through a Celite pad. The filtrate was concentrated and the residue was purified by flash column chromatography on silica gel (230−400 mesh, eluting with 2% EtOAc/toluene) to give the appropriate thiirane derivatives **3** and cyclic disulfides **4** in good yields.

Compound 3b: R_f 0.60 (EtOAc/toluene, 5:95); colorless liquid; yield 0.080 g, 62%; IR (neat) ν_{max} 3279, 1329, 1159, 1093, 813, 665 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 4.73 (t, J = 6.3 Hz, 1H), 3.27 (dd, J = 12.6, 5.4 Hz, 1H), 3.15 (dd, J = 12.6, 7.2 Hz, 1H), 2.49 (s, 1H), 2.43 (s, 3H), 2.33 (s, 1H), 1.61 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.6, 136.8, 129.8, 126.9, 50.4, 44.1, 31.3, 24.2, 21.5; HR-MS m/z calcd for $C_{11}H_{15}NO_2S_2$ [M^+ + Na] 280.0442, found 280.0451.

Compound 3c: R_f 0.30 (EtOAc/hexanes, 3:7); yield 0.085 g, 65%; mp 92 °C; IR (neat) ν_{max} 3280, 1597, 1441, 1324, 1159, 1093, 1050, 813, 664 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74, (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 4.91 (t, J = 6.4 Hz, 1H), 3.29−3.22 (m, 1H), 3.14−3.301 (m, 1H), 2.76−2.72 (m, 2H), 2.42 (s, 3H), 1.44 (d, J = 5.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.6, 136.7, 129.8, 127.0, 46.8, 42.0, 36.4, 21.4, 20.9; HR-MS m/z calcd for $C_{11}H_{15}NO_2S_2$ [M + Na^+] 280.0442, found 280.0475.

Compound 3d: R_f 0.60 (EtOAc/toluene, 5:95); yield 0.088 g, 62%; IR (neat) ν_{max} 3279, 1326, 1159, 1093, 813, 666 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 4.77 (t, J = 6.0 Hz, 1H), 3.35−3.26 (m, 1H), 3.13−3.05 (m, 1H), 2.79 (dd, J = 10.8, 5.1 Hz, 1H), 2.71−2.65 (m, 1H), 2.43 (s, 3H), 1.77−1.68 (m, 1H), 1.54−1.32 (m, 3H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.7, 136.8, 129.8, 127.0, 46.9, 41.7, 40.9, 37.4, 22.2, 21.5, 13.6; HR-MS m/z calcd for $C_{13}H_{19}NO_2S_2$ [M^+ + Na] 308.0755, found 308.0752.

Compound 3e: R_f 0.60 (EtOAc/toluene, 5:95); yield 0.091 g, 61%; IR (neat) ν_{max} 3276, 1326, 1159, 1093, 813, 663 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 4.84 (t, J = 6.0 Hz, 1H), 3.33−3.25 (m, 1H), 3.14−3.05 (m, 1H), 2.79 (dd, J = 11.1, 5.1 Hz, 1H), 2.67 (dd, J = 11.1, 5.4 Hz, 1H), 2.43 (s, 3H), 1.79−1.72 (m, 1H), 1.38−1.33 (m, 5H), 0.89 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.6, 136.8, 129.8, 127.0, 46.9, 41.9, 40.9, 35.1, 31.1, 22.2, 21.5, 13.9; HR-MS m/z calcd for $C_{14}H_{21}NO_2S_2$ [M^+ + Na] 322.0911, found 322.0921.

Compound 3f: R_f 0.60 (EtOAc/toluene, 5:95); yield 0.091 g, 58%; IR (neat) ν_{max} 3275, 1326, 1159, 1094, 813, 664 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 4.75 (t, J = 6.0 Hz, 1H), 3.35−3.27 (m, 1H), 3.13−3.04 (m, 1H), 2.79 (dd, J = 10.5, 5.4 Hz, 1H), 2.68 (dd, J = 10.5, 6.6 Hz, 1H), 2.43 (s, 3H), 1.79−1.70 (m, 1H), 1.40−1.28 (m, 7H), 0.86 (t, J = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.6, 136.7, 128.9, 127.0, 46.9, 41.9, 40.9, 35.3, 31.2, 28.7, 22.5, 21.5, 13.9; HR-MS m/z calcd for $C_{15}H_{23}NO_2S_2$ [M^+ + Na] 336.1068, found 336.1068.

Compound 3g: R_f 0.60 (EtOAc/toluene, 5:95); yield 0.070 g, 52%; IR (neat) ν_{max} 3278, 1324, 1159, 1094, 814, 664 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 4.21 (t, J = 5.4 Hz, 1H), 3.44−3.32 (m, 1H), 3.18−2.89 (m, 3H), 2.44 (s, 3H), 1.99−1.89 (m, 2H), 0.91 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.4, 136.9, 136.3, 129.7, 127.2, 123.1, 39.9, 21.5, 20.6, 13.9; HR-MS m/z calcd for $C_{12}H_{17}NO_2S_3$ [M^+ + Na] 294.0598, found 294.0602.

Compound 3h: R_f 0.60 (EtOAc/toluene, 5:95); yield 0.074 g, 52%; IR (neat) ν_{max} 3280, 1327, 1159, 1094, 814, 665 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 4.92 (t, J = 5.1 Hz, 1H), 3.41−3.33 (m, 1H), 3.16−2.91 (m, 3H), 2.43 (s, 3H), 1.82−1.73 (m, 1H), 1.57−1.26 (m, 3H), 0.94 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.7, 136.8, 129.8, 127.0, 44.4, 41.3, 38.6, 32.4, 22.8, 21.5, 13.6; HR-MS m/z calcd for $C_{13}H_{19}NO_2S_2$ [M^+ + Na] 308.0755, found 308.0763.

Compound 3j: R_f 0.60 (EtOAc/toluene, 5:95); yield 0.087 g, 64%; IR (neat) ν_{max} 3280, 1597, 1325, 1159, 1092, 814, 664 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 4.75 (t, J = 5.4 Hz, 1H), 3.39−3.30 (m, 1H), 3.21−3.13 (m, 1H), 2.91 (t, J = 6.6 Hz, 1H), 2.45 (s, 3H), 1.54 (s, 3H), 1.52 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.7, 136.8, 129.8, 127.4, 67.3, 47.0, 45.1, 30.2, 22.9, 21.7; HR-MS m/z calcd for $C_{12}H_{17}NO_2S_2$ [M^+ + Na] 294.0598, found 294.0604.

Compound 4a: R_f 0.70 (EtOAc/toluene, 5:95); yellow solid; mp 123 °C; yield 0.110 g, 80%; IR (neat) ν_{max} 3265, 1334, 1158, 1092, 814, 664 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 5.23 (d, J = 9.9 Hz, 1H), 4.62−4.56 (m, 1H), 3.09 (dd, J = 11.7, 5.1 Hz, 2H), 2.95 (dd, J = 11.7, 2.4 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.9, 137.6, 129.9, 126.9, 58.7, 44.6, 21.5; HR-MS m/z calcd for $C_{10}H_{13}NO_2S_3$ [M^+ + Na] 298.0035, found 298.0015.

Compound 4b: R_f 0.70 (EtOAc/toluene, 5:95); yellow solid; mp 102 °C; yield 0.023 g, 16%; IR (neat) ν_{max} 3274, 1336, 1162, 1088, 816, 668 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 5.36 (s, 1H), 3.21 (d, J = 11.7 Hz, 2H), 2.93 (d, J = 11.7 Hz, 2H), 2.44 (s, 3H), 1.58 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.6, 139.3, 129.7, 127.1, 68.4, 49.8, 22.6, 21.5; HR-MS m/z calcd for $C_{11}H_{15}NO_2S_3$ [M^+ + Na] 312.0163, found 312.0174.

Compound 4c: R_f 0.40 (EtOAc/hexanes, 3:7); yield 0.023 g, 16%; mp 93 °C; IR (neat) ν_{max} 3274, 2923, 2853, 1743, 1333, 1159, 1091, 813, 666 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 5.05, (d, J = 10.4 Hz, 1H), 4.16−4.12 (m, 1H), 3.42−3.33 (m, 1H), 3.13 (dd, J = 11.6, 4.8 Hz, 1H), 2.89 (dd, J = 11.6, 2.0 Hz, 1H), 2.45 (s, 3H), 1.24 (d, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.9, 137.8, 129.9, 126.9, 64.7, 55.4, 42.2, 21.5, 20.1; HR-MS m/z calcd for $C_{11}H_{15}NO_2S_3$ [M + Na^+] 312.0163, found 312.0169.

Compound 4d: R_f 0.70 (EtOAc/toluene, 5:95); yield 0.025 g, 16%; IR (neat) ν_{max} 3271, 1335, 1159, 1092, 814, 666 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 5.15 (d, J = 10.0 Hz, 1H), 4.23−4.19 (m, 1H), 3.27−3.23 (m, 1H), 3.09 (dd, J = 11.6, 4.8 Hz, 1H), 2.93 (dd, J = 11.6, 2.0 Hz, 1H), 2.46 (s, 3H), 1.49−1.22 (m, 4H), 0.96 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.9, 137.9, 129.9, 126.9, 63.6, 61.3, 42.9, 36.1, 21.5, 21.0, 13.5; HR-MS m/z calcd for $C_{13}H_{19}NO_2S_3$ [M^+ + Na] 340.0476, found 340.0478.

Compound 4f: R_f 0.70 (EtOAc/toluene, 5:95); yield 0.024 g, 14%; IR (neat) ν_{max} 3271, 1336, 1159, 1092, 814, 665 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 5.08 (d, J = 9.9 Hz, 1H), 4.22−4.16 (m, 1H), 3.23−3.17 (m, 1H), 3.08 (dd, J = 11.4, 4.5 Hz, 1H), 2.92 (dd, J = 11.4, 1.8 Hz, 1H), 2.44 (s, 3H), 1.47−1.16 (m, 8H), 0.86 (t, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.9, 137.9, 129.9, 126.9, 63.5, 61.6, 42.9, 34.0, 31.2, 27.5, 22.4, 21.5, 13.9; HR-MS m/z calcd for $C_{15}H_{23}NO_2S_3$ [M^+ + Na] 368.0789, found 368.0800.

Compound 4g: R_f 0.70 (EtOAc/toluene, 5:95); yield 0.020 g, 13%; IR (neat) ν_{max} 3274, 1336, 1158, 1092, 814, 667 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 5.07 (d, J = 10.2 Hz, 1H), 4.43−4.37 (m, 1H), 3.45−3.39 (m, 1H), 3.11 (dd, J = 11.4, 3.9 Hz, 1H), 2.78 (dd, J = 11.4, 2.1 Hz, 1H), 2.44 (s, 3H), 1.88−1.62 (m, 2H), 0.97 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.8, 138.1, 129.9, 126.9, 61.9, 59.9, 43.2, 22.2, 21.5, 13.6; HR-MS m/z calcd for $C_{12}H_{17}NO_2S_3$ [M^+ + Na] 326.0319, found 326.0334.

Compund 4h: R_f 0.70 (EtOAc/toluene, 5:95); yield 0.021 g, 13%; IR (neat) ν_{max} 3271, 1335, 1157, 1092, 814, 664 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 5.10 (d, J = 10.2 Hz, 1H), 4.41−4.34 (m, 1H), 3.51−3.45 (m, 1H), 3.12 (dd, J = 11.1, 4.2 Hz, 1H), 2.81 (dd, J = 11.1, 1.8 Hz, 1H), 2.44 (s, 3H), 1.77−1.52 (m, 2H), 1.38−1.26 (m, 2H), 0.86 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.8, 138.1, 129.9, 126.9, 60.2, 59.9, 43.1, 30.9, 22.5, 21.5, 13.9; HR-MS m/z calcd for $C_{13}H_{19}NO_2S_3$ [M^+ + Na] 340.0476, found 340.0483.

Compound 4i: R_f 0.70 (EtOAc/toluene, 5:95); yield 0.087 g, 60%; IR (neat) ν_{max} 3281, 1336, 1158, 1091, 1048, 814, 665 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 5.05 (d, J = 10.2 Hz, 1H), 4.35−4.28 (m, 1H), 3.64−3.56 (m, 1H), 3.15 (dd, J = 11.4, 4.5 Hz, 1H), 2.81 (dd, J = 11.4, 1.8 Hz, 1H), 2.44 (s, 3H), 1.33 (d, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.6, 143.8, 129.9, 126.9, 61.9, 53.9, 43.2, 21.6, 13.8; HR-MS m/z calcd for $C_{11}H_{15}NO_2S_3$ [M^+ + Na] 312.0163, found 312.0173.

Compound 4j: R_f 0.70 (EtOAc/toluene, 5:95); yield 0.024 g, 16%; mp 108 °C; IR (neat) ν_{max} 3276, 1327, 1159, 1092, 813, 671 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 4.97 (d, J = 10.2 Hz, 1H), 3.90−3.84 (m, 1H), 3.19 (dd, J = 10.8, 4.8 Hz, 1H), 2.78 (dd, J = 10.8, 2.7 Hz, 1H), 2.44 (s, 3H), 1.41 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.8, 137.9, 129.9, 126.9, 66.7, 61.9, 41.0, 27.5, 22.2, 21.5; HR-MS m/z calcd for $C_{12}H_{27}NO_2S_3$ [M^+ + Na] 326.0319, found 326.0328.

Compound 15: R_f 0.60 (EtOAc/toluene, 5:95); yellow solid; mp 152 °C; yield 0.123 g, 78%; IR (neat) ν_{max} 3264, 1333, 1168, 1061, 1031, 888, 821, 684 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 5.41 (d, J = 7.6 Hz, 1H), 4.00−3.97 (m, 1H), 3.56 (d, J = 2.0 Hz, 2H), 2.43 (s, 3H), 2.33−2.22 (m, 2H), 2.05−1.93 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.2, 139.3, 130.1, 127.1, 62.2, 47.5, 27.2, 21.6, 16.5; HR-MS m/z calcd for $C_{13}H_{17}NO_2S_3$ [M^+ + Na] 338.0319, found 338.0329.

Compound 16: R_f 0.60 (EtOAc/toluene, 5:95); colorless solid; mp 148 °C; yield 0.111 g, 75%; IR (neat) ν_{max} 3270, 1332, 1161, 1071, 1038, 897, 810, 669 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, J = 8.1 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 5.22 (d, J = 9.8 Hz, 1H), 4.22 (dd, J = 9.9, 5.9 Hz, 1H), 3.29 (t, J = 5.0 Hz, 1H), 2.43 (s, 3H), 2.21−2.14 (m, 1H), 1.88−1.76 (m, 2H), 1.69−1.61 (m, 3H), 1.14 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.8, 138.0, 129.8, 126.9, 61.8, 58.5, 47.9, 29.2, 26.2, 21.5, 20.6, 16.3; HR-MS m/z calcd for $C_{14}H_{19}NO_2S_2$ [M^+ + Na] 320.0755, found 320.0766.

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Supporting Information Available: ^1H, ^{13}C spectra for all new compounds and X-ray crystallographic data for compounds **3c**, **4c**, **4j**, **15**, and **16**. This material is available free of charge via the Internet at http://pubs.acs.org.