HETEROCYCLES, Vol. 75, No. 10, 2008, pp. 2415 - 2420. © The Japan Institute of Heterocyclic Chemistry
Received, 17th April, 2008, Accepted, 22nd May, 2008, Published online, 26th May, 2008. COM-08-11412

SYNTHESIS AND PROPERTIES OF *S*-AMINOTHIIRANIUM SALTS OF *anti*- AND *syn*-9,9'-BIBENZONORBORNENYLIDENES AND 2,2'-BIADAMANTYLIDENE†

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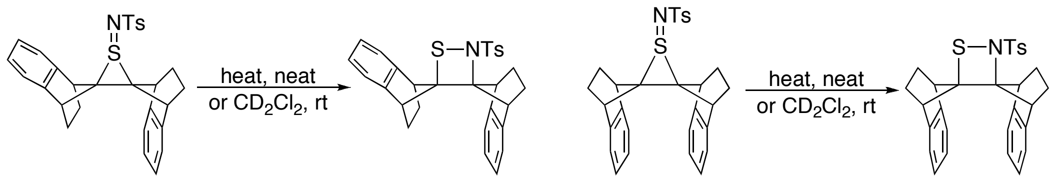
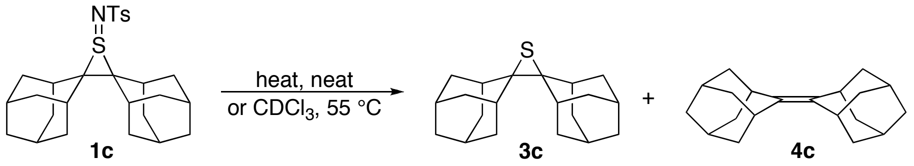
Abstract – *S*-Aminothiiranium salts **5a–c** of *anti*- and *syn*-9,9'-bibenzonorbornenylidenes and 2,2'-biadamantylidene were synthesized by reacting thiiranes **3a–c** with *O*-mesitylenesulfonylhydroxylamine. Decomposition of **5a** and **5c** in CD_2Cl_2 at rt yielded a mixture of the corresponding alkenes and thiiranes, whereas that of **5b** yielded 1,2-thiazetidin-2-ium salts **8b**. A CH_2Cl_2 solution of **8b** was treated briefly with aq. $NaHCO_3$ at 0 °C to produce *N*-unsubstituted 1,2-thiazetidine**10b**.

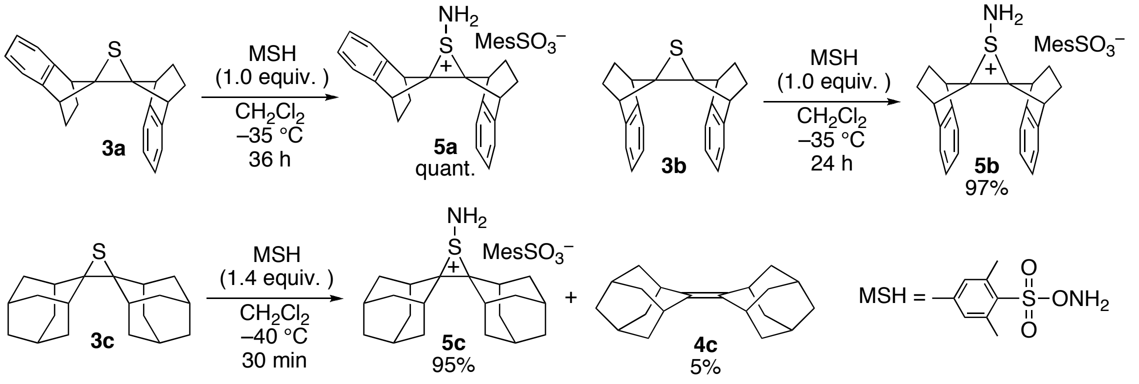
Recently, sulfimide and related compounds have attracted much attention from the viewpoint of synthesis, structure, reactions, and synthetic applications.[1] *S*-Aminosulfonium salt is a key intermediate in the synthesis of *N*-unsubstituted sulfimide.[2] Although some *S*-aminosulfonium salts have been reported thus far,[2,3] three-membered *S*-aminothiiranium salts have not been reported. In order to better understand the chemistry of sulfimides, study of thiirane 1-imides and *S*-aminothiiranium salts is of crucial importance. Recently, we succeeded in isolating *N*-tosyl thiirane 1-imide **1** for the first time,[4] by taking advantage of substituent effects.[5,6] Ring-enlargement of **1a** and **1b** occurred easily with retention of the configuration of the original stereochemistry to yield 1,2-thiazetidines, **2a** and **2b**, respectively, whereas **1c** decomposed to yield a mixture of the corresponding alkene **3c** and thiirane **4c**. We report here the synthesis and properties of novel *S*-aminothiiranium salts.



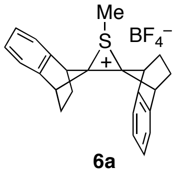
1a **2a** **1b** **2b**



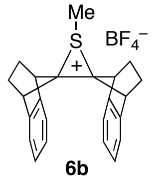
Thiiranes **3a–c** reacted with *O*-mesitylenesulfonylhydroxylamine (MSH)[2] at low temperature to produce the corresponding *S*-aminothiiranium salts **3a–c** in good yields. Thus, the reaction of *anti*-thiirane **3a** with one molar equivalent of MSH in CH_2Cl_2 at −40 °C, followed by the removal of CH_2Cl_2 under reduced pressure at the same temperature yielded **5a** quantitatively.[7] Following the same procedure with *syn*-thiirane **3b** produced **5b** in 97% yield.[7] The reaction of 2,2'-adamantylidene sulfide **3c** with MSH at −40 °C, followed by crystallization due to the addition of pentane at the same temperature, and subsequent filtration produced **5c** in 95% yield.[7] Evaporation of the resulting filtrate produced compound **4c** in 5% yield.



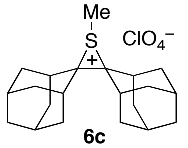
From the results of ^{13}C NMR spectra, the sulfur atom in **5** is found to have a pyramidal structure. The thiirane-ring carbon signals of **5** (**5a**: δ 94.3, 94.6, **5b**: δ 89.5, **5c**: δ 96.9) showed downfield shifts relative to those of the corresponding *S*-methylthiiranium salts **6** (**6a**: δ 88.6, 89.0, **6b**: δ 83.7, **6c**: δ 92.3)[6,8] and *N*-tosyl thiirane 1-imides **1** (**1a**: δ 82.8, 83.7, **1b**: δ 79.9, **1c**: δ 77.3),[4] suggesting that the C–S bond electrons of the ring in **5** must be drawn more towards the positively charged pyramidal sulfur atom, compared with those in **6** and **1**. The FAB mass spectra showed the peaks due to the corresponding *S*-aminothiiranium ions **7a** and **7b** at *m/Z* 332 for **5a** and **5b** and that due to **7c** at *m/Z* 316 for **5c**. The IR spectrum in Nujol showed N–H stretching absorption in the range of 3200–3166 cm^{-1} and asymmetric and symmetric S=O stretching absorptions of MesSO$_3^-$ around 1180 and 1085 cm^{-1}, respectively.



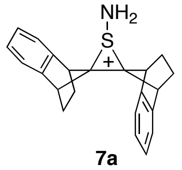
6a



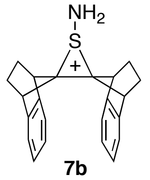
6b



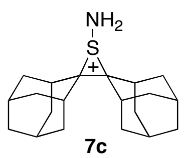
6c



7a

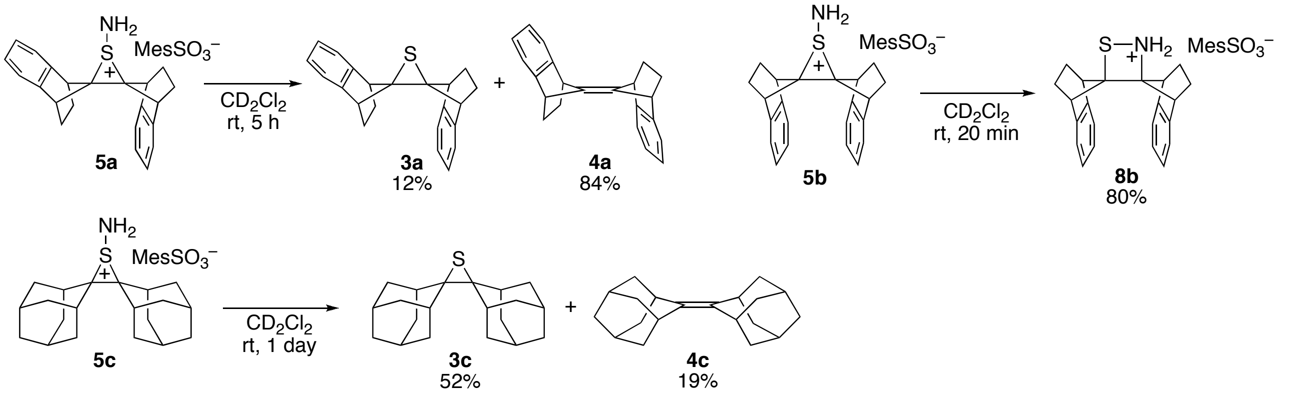


7b

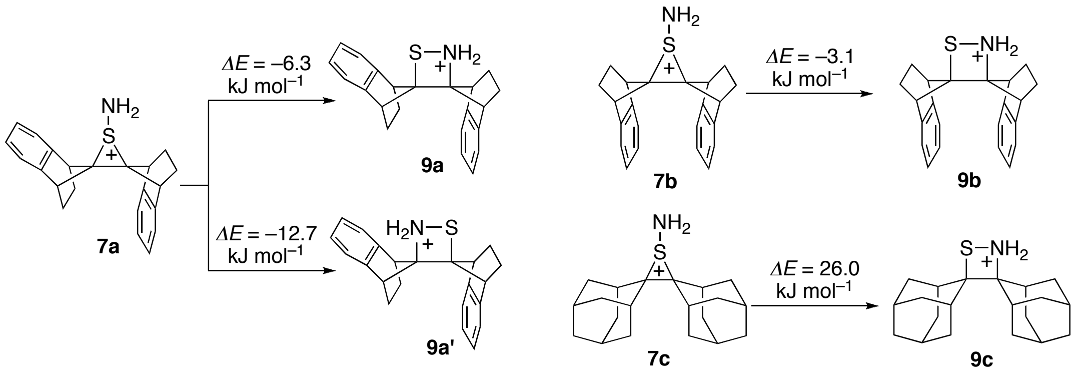


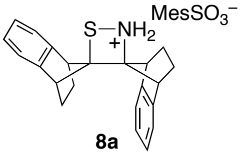
7c

The *S*-aminothiiranium salt **5** is labile in solution even at rt, similar to **1**. In fact, keeping CD_2Cl_2 solutions of **5a** and **5c** at rt yielded a mixture of the corresponding thiiranes and alkenes. In contrast, the reaction of **5b** in CD_2Cl_2 proceeded with retention of the configuration of the original stereochemistry to produce 1,2-thiazetidin-2-ium salt **8b** in 80% yield.[9] The progress of the decomposition of **5c** in CD_2Cl_2 was monitored from −15 to 5 °C by ^{1}H NMR. The formation of **3c** and **4c** obeyed first-order kinetics in the initial stage, but not in the later stage, suggesting that other products containing nitrogen would accelerate the formation.

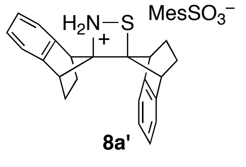


Optimized structures of **7** and 1,2-thiaztidin-2-ium ion **9** were determined from theoretical calculations.[10] The calculations predict that **9a** and **9a'** are thermally more stable than **7a** by 6.3 and 12.7 kJ mol^{-1} respectively, and **9b** is more stable than **7b** by 3.1 kJ mol^{-1}, whereas **9c** is less stable than **7c** by 26.0 kJ mol^{-1}, probably due to steric repulsion between the two adamantylidene groups of **9c**. Thus, the formation of **8a** and **8a'** from **5a** and that of **8b** from **5b** are favorable exothermic processes, but the formation of **8c** from **5c** is unfavorable. Therefore, for **5c**, a nucleophile such as H_2O, which might be present as an impurity and a nitrogen-containing product would attack its nitrogen and pyramidal sulfur atoms to form **3c** and **4c**, respectively. Neither **8a** nor **8a'** was observed in the decomposition of **5a** because the energy level of the transition state to **8a** and **8a'** is probably much higher than that to **8b**.

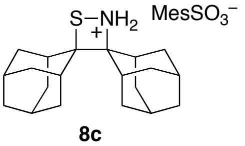




8a

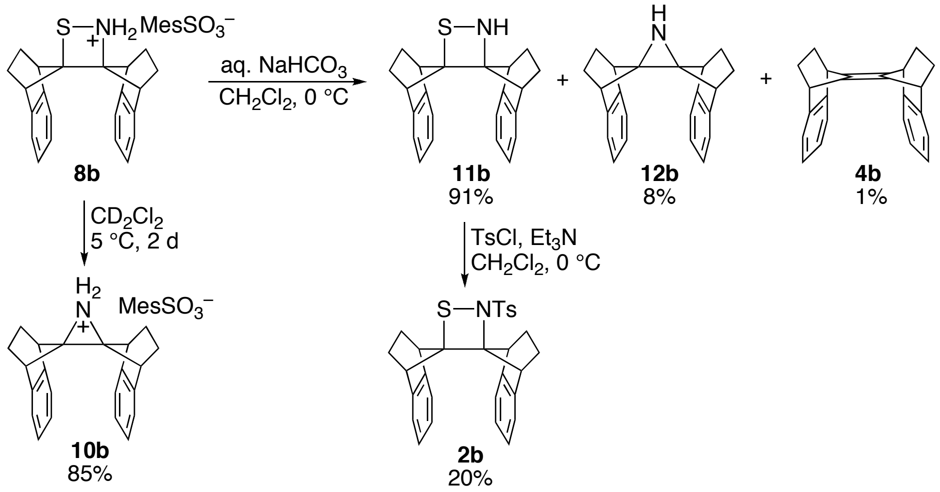


8a'

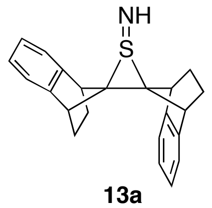


8c

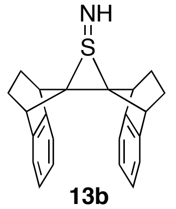
The salt **8b** is less stable in solution than **2b**. Thus, keeping a CH_2Cl_2 solution of **8b** at 5 °C for two days produced aziridinium salt **10b** in 85% yield. The same solution was treated briefly with aq. $NaHCO_3$ at 0 °C to produce **11b**, the first *N*-unsubstituted 1,2-thiazetidine,[4,11,12] in 91% yield along with aziridine **12b** and **4b** in 8% and 1% yields, respectively. Reaction of **11b** and TsCl with Et_3N produced **2b** in 20% yield.[4]



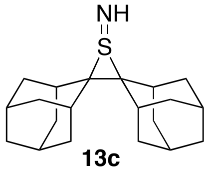
The isolation of *N*-unsubstituted thiirane 1-imides **13a–c** was not successful. Brief treatment of **5a** in CH_2Cl_2 with aq. $NaHCO_3$ at 0 °C yielded **3a** quantitatively, whereas similar treatment of **5b** and **5c** yielded a mixture of the corresponding thiiranes and alkenes.



13a



13b



13c

ACKNOWLEDGEMENTS

This work was supported by Grants-in-Aid for Scientific Research from Japan Society for the Promotion of Science (Nos. 13740748 and 15550026).

REFERENCES AND NOTES

†Dedicated to Prof. Keiichiro Fukumoto on the occasion of his 75th birthday.

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7. **5a**: ^{1}H NMR (CD_2Cl_2, –35 °C) δ 1.04—1.32 (m, 4H), 1.43—1.65 (m, 2H), 2.26 (s, 3H), 2.40—2.72 (m, 2H), 2.57 (s, 6H), 3.37—3.45 (m, 1H), 3.47—3.55 (m, 1H), 3.82—3.93 (m, 1H), 3.97—4.05 (m, 1H), 4.79 (s, 2H), 6.87 (s, 2H), 7.14—7.42 (m, 8H); ^{13}C NMR (CD_2Cl_2, –35 °C) δ 20.4, 22.8, 23.5, 25.3, 25.6, 26.0, 44.7, 45.2, 45.7, 47.1, 94.3, 94.6, 120.7, 120.9, 121.0, 121.4, 127.1, 127.7, 127.9, 136.4, 140.2, 142.5, 142.8, 142.9; IR (Nujol) 3166 ($–NH_2$), 1176, 1084 ($>SO_2$) cm^{-1}; MS (FAB) *m*/*Z* 332 [$(M–MesSO_3)^+$]. **5b**: ^{1}H NMR (CD_2Cl_2, –35 °C) δ 1.35—1.51 (m, 4H), 2.28 (s, 3H), 2.33—2.43 (m, 2H), 2.43—2.54 (m, 2H), 2.69 (s, 6H), 3.27—3.35 (m, 2H), 3.67—3.78 (m, 2H), 5.54 (s, 2H), 6.72—6.89 (m, 8H); ^{13}C NMR (CD_2Cl_2, –35 °C) δ 21.1, 23.5, 26.2, 26.5, 46.3, 47.7, 89.5, 121.2, 121.3, 127.3, 127.6, 131.0, 137.2, 139.1, 140.0, 142.2, 142.7; IR (Nujol) 3200 ($–NH_2$), 1180, 1085 ($>SO_2$) cm^{-1}; MS (FAB) *m*/*Z* 332 [$(M–MesSO_3)^+$]. **5c**: ^{1}H NMR (CD_2Cl_2, –40 °C) δ 1.71—2.19 (m, 26H), 2.24 (s, 3H), 2.41 (s, 2H), 2.58 (s, 6H), 4.99 (s, 2H), 6.85 (s, 2H); ^{13}C NMR (CD_2Cl_2, –25 °C) δ 20.5, 22.8, 26.3, 26.7, 28.3, 31.5, 36.0, 36.1, 36.9, 37.8, 37.9, 96.9, 130.3, 136.6, 138.4, 139.4; IR (Nujol) 3174 ($–NH_2$), 1179, 1086 ($>SO_2$) cm^{-1}; MS (FAB) *m*/*Z* 316 [$(M–MesSO_3)^+$].
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9. **8b**: ^{1}H NMR (CD_2Cl_2, –35 °C) δ 0.85—0.97 (m, 2H), 0.97—1.08 (m, 2H), 1.59—1.72 (m, 2H), 2.24—2.30 (m, 2H), 2.33 (s, 3H), 2.81 (s, 6H), 3.44 (s, 2H), 3.65 (s, 2H), 6.42—6.56 (m, 4H), 6.74—6.85 (m, 4H), 7.04 (s, 2H), 10.46 (s, 2H); ^{13}C NMR (CD_2Cl_2, –35 °C) δ 21.1, 23.7, 24.4, 25.9, 47.9, 49.3, 78.2, 91.8, 120.5, 120.9, 127.0, 127.6, 131.4, 137.5, 138.7, 140.1, 140.9, 142.2; IR (Nujol) 2649-2524 (br, $>NH_2^+$), 1595 ($>NH_2^+$), 1142, 1085 ($>SO_2$) cm^{-1}; MS (FAB) *m/Z* 332 $[(M\text{-}MesSO_3)^+]$.
10. The calculations have performed by using the Gaussian 98 program [B3LYP/6-31G(d) level] on personal computers running RedHat Linux 7.2. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1998. Gaussian 98, Revision A.7.
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12. **11b**: ^{1}H NMR (CD_2Cl_2, 0 °C) δ 0.68—0.77 (m, 2H), 0.78—0.85 (m, 2H), 1.63—1.75 (m, 2H), 1.84—1.94 (m, 2H), 3.23 (br s, 2H), 3.27—3.33 (m, 2H), 6.37—6.45 (m, 4H), 6.62—6.69(m, 4H); ^{13}C NMR (CD_2Cl_2, 0 °C) δ 25.2, 26.3, 48.6, 49.2, 83.1, 90.8, 120.2, 120.5, 126.37, 126.38, 143.5, 143.8; IR (Nujol) 3225 ($>NH$) cm^{-1}; MS (FAB) *m/Z* 332 (MH^+).