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SYNTHESIS AND THERMAL DECOMPOSITION OF THIIRANE 1-IMIDES OF 2'-ADAMANTYLIDENE-9-BENZONORBORNENYLIDENE

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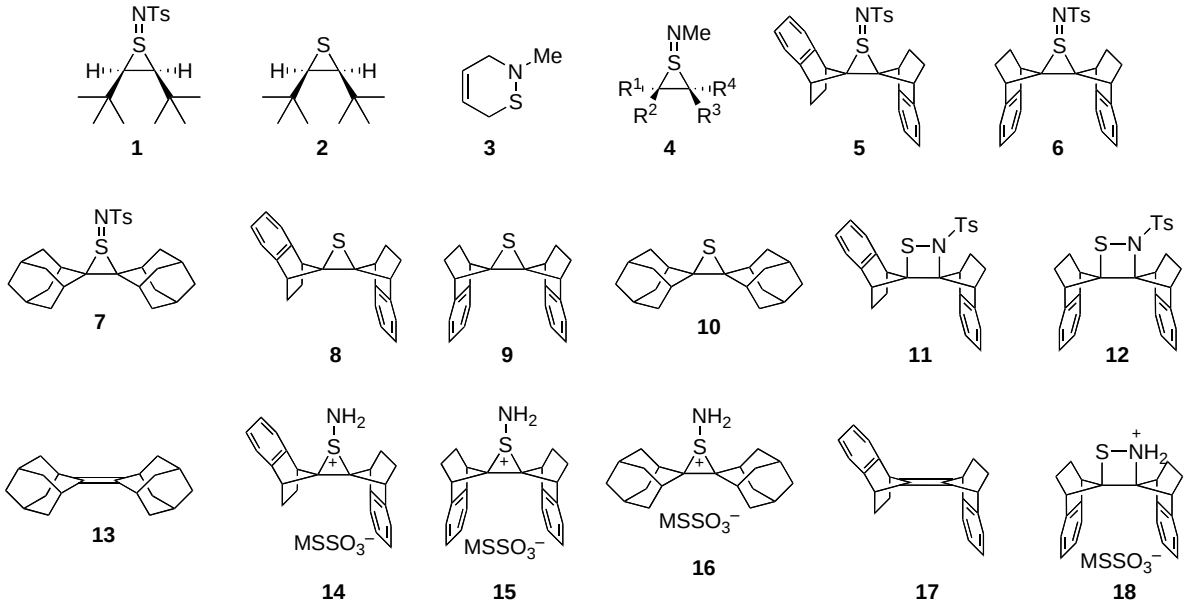
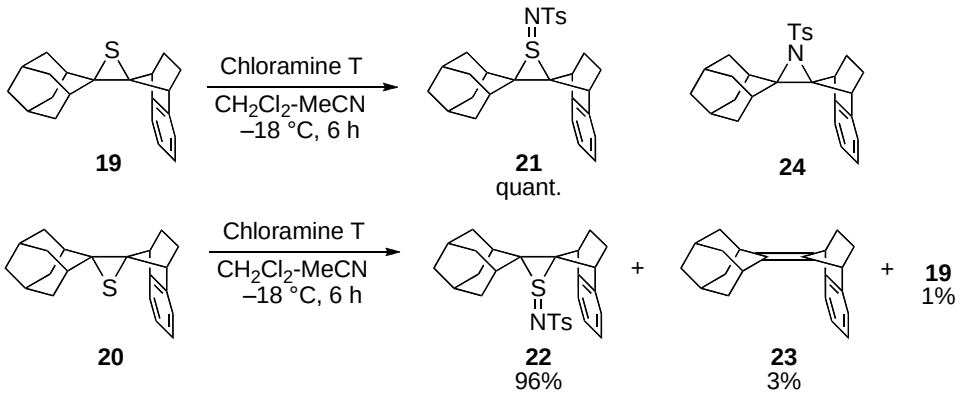
Abstract – Two isolable thiirane 1-imides **21** and **22** were synthesized successfully by imination of *anti*- and *syn*-2'-adamantylidene-9-benzonorbornenylidene sulfides **19** and **20** with Chloramine T in CH_2Cl_2 and MeCN at −18 °C. Thermal decompositions of **21** and **22** in solution at room temperature or in the solid state on heating gave mainly **19**, alkene **23**, and aziridine **24**.

The chemistry of thiiranes and their 1-oxides has been extensively investigated from the viewpoint of synthesis, structure, reactions, and synthetic application to useful compounds.[1] Nevertheless, only a few studies have dealt with the chemistry of thiirane 1-imides.[2,3,4] Kellogg and coworkers reported the attempted synthesis of *N*-tosylthiirane 1-imide **1**.[2] Although *cis*-thiirane **2** reacted with tosyl azide in the presence of Cu powder in MeOH or with Chloramine T in water, no thiirane 1-imide was observed. Hata and Watanabe reported that thiirane reacted with oxaziridine and 1,3-butadiene at room temperature to give cycloadduct **3**.[3] For the reaction pathway, it was speculated that *N*-methylthiirane 1-imide **4** forms in the initial stage, and then decomposes into the corresponding alkene and MeN=S, which is trapped by butadiene to finally give **3**. Jenks and coworkers used computational methods to estimate the bond dissociation enthalpies of the S–N bond for the parent thiirane 1-imide, which are about 40 kcal mol^{-1} lower than those of the S–O bond for the parent thiirane 1-oxide.[4] Recently, we succeeded in the first isolation of thiirane 1-imides **5**–**7**,[5] which were synthesized successfully by imination of the corresponding thiiranes **8**–**10** with Chloramine T (TsNNaCl) in a mixed solvent of CH_2Cl_2 and MeCN. Stereospecific ring-enlargement of **5** and **6** proceeded to form **11** and **12**, respectively, in solution at room temperature or in the solid state on heating, whereas **7** decomposed on heating to form a mixture of **10** and **13**. Decomposition of *S*-aminothiiranium salt **15**, which was synthesized by reaction of **9** with $MSSO_3NH_2$, gave **18**, whereas those of **14** and **16** afforded a mixture of the corresponding alkanes and

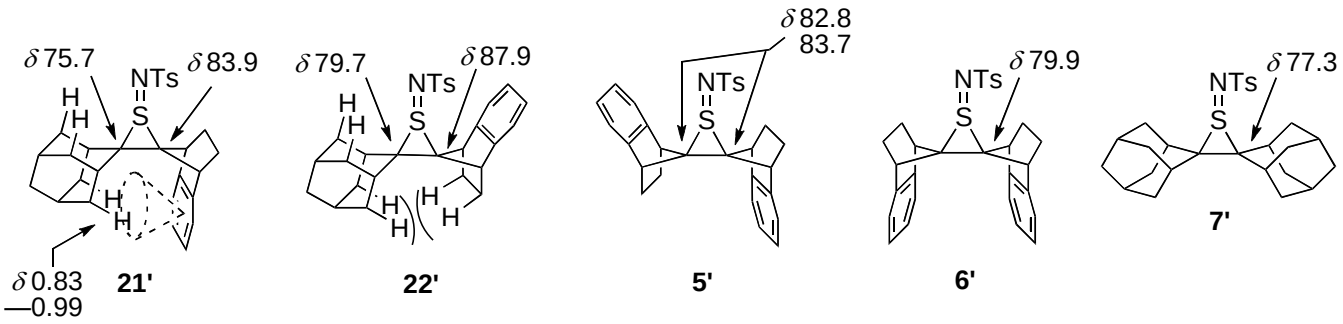
thiiranes.[6] The decomposition products seemed to strongly depend on the substituents connecting with the thiirane ring. Here, we report the synthesis and thermal decomposition of thiirane 1-imides of 2'-adamantylidene-9-benzonorbornenylidene.



Thiirane 1-imides **21** and **22** were synthesized from the corresponding thiiranes **19** and **20**,[7] respectively, by methods similar to the synthesis of **5**–**7**.[5] Thus, **19** and **20** reacted with 1.5 molar equivalent of Chloramine T in CH_2Cl_2-MeCN (3:1) at −18 °C. After a cold aqueous $NaHCO_3$ solution was added to the reaction mixture, the organic layer was separated, dried over K_2CO_3, and evaporated under reduced pressure at 0 °C. The thiirane 1-imide **21** was obtained quantitatively in the imination of **19**. Recrystallization of **21** from CH_2Cl_2 and hexane at rt resulted in the decomposition to **19**, alkene **23**, and aziridine **24** in 23%, 73%, and 4% yields, respectively, together with $TsNH_2$ in 81% yield, whereas that at –18 °C afforded **21** as colorless crystals in the pure form, mp 107.0−108.0 °C (dec.). The residue for the reaction of **20** consisted of a mixture of **22**, **23**, and **19** in the ratio of 96:3:1. Purification of the mixture by recrystallization from CH_2Cl_2 and hexane at –18 °C gave **22**, mp 94.0−95.0 °C (dec.), in 52% yield. The concentration of the mother liquor of this recrystallization at –18 °C yielded a mixture of **22**, **23**, and **19** in the ratio of 93:6:1.



The stereochemistry of **21** and **22** could be determined easily by ^{1}H NMR.[7,8] Thus, the two hydrogen atoms of the methylenes of **21**, which face the benzene ring and hence are under the influence of the ring current effect,[7] appeared as a multiplet in the region of δ 0.83−0.99. This multiplet is a higher field than any multiplet in the region of δ 1.58−2.35 assigned to the corresponding methylene hydrogens of **22**. On the other hand, the ^{13}C NMR spectra at –20 °C showed fifteen sp^3 and ten sp^2 carbon peaks for **21**[9] and sixteen sp^3 and ten sp^2 carbon peaks for **22**. The carbon signals of the thiirane ring of **22** (δ 79.7, 87.9) appeared at lower fields than those of **21** (δ 75.7, 83.9), **5** (δ 82.8, 83.7), **6** (δ 79.9), and **7** (δ 77.3), suggesting that steric repulsion among the substituents of **22**, which causes the thiirane ring to be strained, is more severe than for those of **21** and **5**−**7**.[10] The IR spectra showed strong S–N stretching absorption at 970 cm^{-1} for **21** and 967 cm^{-1} for **22**. These values were similar to the corresponding absorption for **5**−**7** (**5**: 970, **6**: 957, **7**: 961 cm^{-1}).[5]

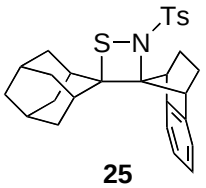


Both **21** and **22** decomposed in solution at room temperature, or in the solid state on heating (Table 1). Thus, allowing a $CDCl_3$ solution of **21** to stand at room temperature for 10 days gave **19**, **23**, and **24** in 36%, 59%, and 5% yields, respectively, and that of **22** afforded **19**, **23**, and **24** in 19%, 75%, and 4% yields, respectively, together with **20** in 2% yield. When CD_2Cl_2 was used, each **21** and **22** decomposed to

Table 1. Decompositions of the thiirane 1-Imides **21** and **22**

21 or **22** ⟶ **19** + **20** + **23** + **24**

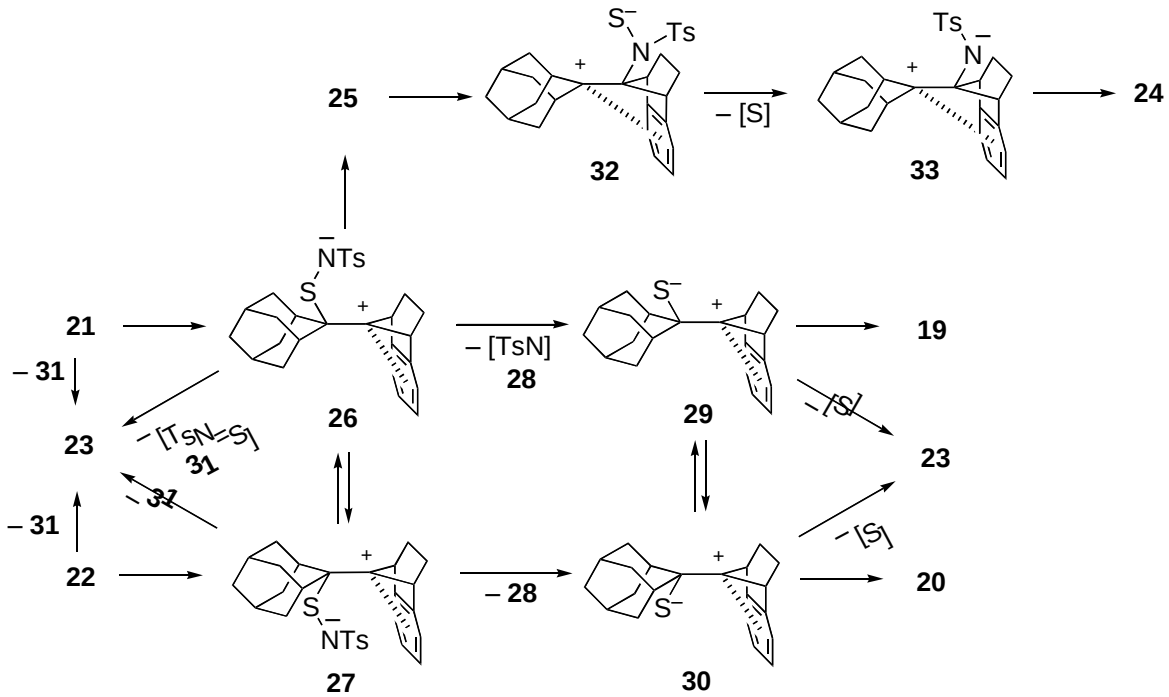
thiirane 1-imide	conditions	yield (%) **19**	**20**	**23**	**24**
21	$CDCl_3$, 25 °C, 10 d	36	—	59	5
22	$CDCl_3$, 25 °C, 10 d	19	2	75	4
21	CD_2Cl_2, 25 °C, 10 d	55	—	37	8
22	CD_2Cl_2, 25 °C, 10 d	50	2	41	7
21	neat, 110 °C, 5 h	55	—	18	27
22	neat, 100 °C, 5 h	43	2	39	16



an approximately 7:5:1 mixture of **19**, **23**, and **24**. In the case of **22**, **20** was also produced. Changing $CDCl_3$ for CD_2Cl_2 increased the ratio of **19** to **23**. On the other hand, heating each **21** and **22** without solvent to near their decomposition point gave **19** as a major product, and the proportion of **24** was larger compared with the decomposition in solution. The aziridine **24** seemed to be formed through 1,2-thiazetidine intermediate **25**. Interestingly, the decomposition of **21** proceeded with retention of the

configuration of the original stereochemistry, whereas that of **22** primarily showed an inversion of its configuration.

A possible mechanism of the thermal decompositions is as follows. In case of **21**, the C−S bond that faces the benzene ring is cleft to form carbenium salt **26**,[11] where the neighboring group participation of the benzene ring not only assists the bond cleavage, but also stabilizes the carbocation by homoconjugation.[12] The salt **26** undergoes extrusion of tosyl nitrene **28** to form carbenium salt **29**, which then transforms to **19** by the C−S bond formation. Similarly, the pathway of **22**, in which the C−S bond is easily broken by steric repulsion among the substituents, proceeds through **27** and then **30** to form **20**. The alkene **23** is produced by several reactions such as releasing reactive species **28** and TsN=S **31**[13] from **21** and **22** and from **26** and **27**,[3] respectively, and desulfurizing **29** and **30**. These reactions must be accelerated by the action with the resulting reactive species and H_2O as an impurity. The extrusion of **31** from **21** and **22** follows a pathway similar to that of intermediary SO[14] from thiirane 1-oxides.[15] The equilibrium between **26** and **27** and that between **29** and **30** proceed through rotation about their C−C bond. The C−N bond formation in **26** gives 1,2-thiazetidine **25**, which is unstable by steric repulsion among the substituents. The C−S bond cleavage with the assistance of the neighboring group participation results in the formation of carbenium salt **32**, which is then desulfurized to form carbenium salt **33**. The C−N bond formation of **33** affords **24**. The reason why the original stereochemistry is retained in the decompositions of **21** but is inverted for **22** must be the steric repulsion among the substituents, which shifts the equilibria to **26** and **29**, and the homoconjugation of the carbocation with the benzene ring in **26** and **29**, causing the sp^2 face opposite to the benzene ring to be more reactive than the other.



ACKNOWLEDGEMENTS

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REFERENCES AND NOTES

1. I. A. Abu-Yousef and D. N. Harpp, *J. Sulfur Chem.*, 1997, **20**, 1; D. C. Dittmer, 'Comprehensive Heterocyclic Chemistry,' Vol. 7, ed. by E. D. Lwowski, Pergamon, Oxford, 1984, p. 131; H. Hart, 'Comprehensive Heterocyclic Chemistry,' Vol. 7, ed. by E. D. Lwowski, Pergamon, Oxford, 1984, p. 18; W. Ando, N. Choi, and N. Tokitoh, 'Comprehensive Heterocyclic Chemistry II,' Vol. 1A, ed. by A. R. Katritzky, C. W. Rees, and E. F. V. Scriven, Pergamon, Oxford, 1996, p. 173; S. R. Harring, T. Livinghouse, 'Comprehensive Heterocyclic Chemistry II,' Vol. 1A, ed. by A. R. Katritzky, C. W. Rees, and E. F. V. Scriven, Pergamon, Oxford, 1996, p. 241.
2. P. Raynolds, S. Zonnebelt, S. Bakker, and R. M. Kellogg, *J. Am. Chem. Soc.*, 1974, **96**, 3146.
3. Y. Hata and M. Watanabe, *J. Org. Chem.*, 1980, **45**, 1691.
4. S. A. Stoffregen, R. D. McCulla, R. Wilson, S. Cercone, J. Miller, and W. S. Jenks, *J. Org. Chem.*, 2007, **72**, 823.
5. Y. Sugihara, Y. Aoyama, H. Okada, and J. Nakayama, *Chem. Lett.*, 2008, **37**, 658.
6. Y. Sugihara, R. Ohtsu, and J. Nakayama, *Heterocycles*, 2008, **75**, 2415.
7. Y. Sugihara, A. Kobiki, and J. Nakayama, *Heterocycles*, 2009, **78**, 103.
8. **21**: colorless crystals (CH_2Cl_2/hexane); mp > 107 °C (dec.); ^{1}H NMR (400 MHz, −20 °C): δ 0.83−0.99 (m, 2H), 1.35−1.43 (m, 1H), 1.47−1.54 (m, 2H), 1.55−1.74 (m, 6H), 1.75−1.86 (m, 2H), 1.90 (br s, 1H), 1.96−2.04 (m, 1H), 2.22−2.36 (m, 2H), 2.41 (s, 3H), 2.47 (br s, 1H), 3.25−3.32 (m, 1H), 3.88−3.97 (m, 1H), 7.15−7.33 (m, 6H), 7.80−7.88 (m, 2H). ^{13}C NMR (101 MHz, −20 °C): δ 21.4, 25.3, 25.8, 26.0, 26.2, 28.8, 33.6, 33.7, 35.0, 35.5, 35.6 (2C), 43.1, 44.0, 75.7, 83.9, 120.7, 120.9, 125.5, 127.0, 127.3, 129.1, 141.1, 141.3, 141.8, 144.2; IR (KBr): 3040, 2982, 2931, 2853, 1469, 1445, 1295, 1140, 1088, 970, 810, 767, 740 cm^{-1}. Anal. Calcd for $C_{28}H_{31}NO_2S_2$: C, 70.40; H, 6.54; N, 2.93. Found: C, 70.29; H, 6.52; N, 2.90. **22**: colorless crystals (CH_2Cl_2/hexane); mp > 94 °C (dec.); ^{1}H NMR (400 MHz, −20 °C): δ 1.58−1.66 (m, 1H), 1.67−1.76 (m, 2H), 1.78−1.97 (m, 6H), 2.05−2.17 (m, 4H), 2.23−2.35 (m, 4H), 2.32 (s, 3H), 2.69 (br s, 1H), 3.32−3.36 (m, 1H), 4.08−4.14 (m, 1H), 6.94−6.97 (m, 2H), 7.14−7.24 (m, 3H), 7.24−7.26 (m, 2H), 7.28−7.34 (m, 2H). ^{13}C NMR (101 MHz, −20 °C): δ 21.4, 25.0, 26.4, 26.6, 27.8, 28.5, 33.1, 34.1, 36.2, 37.0, 37.5, 38.1, 44.1, 45.6, 79.7, 87.9, 120.9, 121.4, 125.6, 126.3, 126.7, 128.8, 140.8, 141.2, 143.6, 145.4; IR (KBr): 3018, 2984, 2936, 2855, 1470, 1452, 1278, 1134, 1084, 967, 942, 821, 780, 769, 736 cm^{-1}.
9. The signal at δ 35.6 is due to a degeneracy of two carbon signals.

10. E. Breimaier and W. Voelter, *Carbon-13 NMR Spectroscopy*, 3rd ed., VCH, Weinheim, 1987, p. 186; N. J. Jacobsen, *NMR Spectroscopy Explained*, Wiley-Interscience, Hoboken, 2007, p. 29.
11. S. Oae, T. Aida, and N. Furukawa, *J. Chem. Soc., Perkin Trans. 2*, 1974, 1231; T. Aida, N. Furukawa, and S. Oae, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1432.
12. K. Okada and T. Mukai, *J. Am. Chem. Soc.*, 1978, **100**, 6509; L. A. Paquette, L. W. Hertel, R. Gleiter, and M. Böhm, *J. Am. Chem. Soc.*, 1978, **100**, 6510; L. A. Paquette, L. W. Hertel, R. Gleiter, M. C. Böhm, M. A. Beno, G. G. Christoph, *J. Am. Chem. Soc.*, 1981, **103**, 7106; Y. Sugihara, K. Noda, and J. Nakayama, *Tetrahedron Lett.*, 2000, **40**, 8907; Y. Sugihara, K. Noda, and J. Nakayama, *Tetrahedron Lett.*, 2000, **40**, 8911; K. Noda, Y. Sugihara, and J. Nakayama, *Heteroatom Chem.*, 2001, **12**, 625.
13. O. Meth-Cohn and G. Vuuren, *J. Chem. Soc., Perkin Trans. 1*, 1986, 245.
14. J. Nakayama, Y. Tajima, P. Xue-hua, and Y. Sugihara, *J. Am. Chem. Soc.*, 2007, **129**, 7250.
15. G. E. Hartzell and J. N. Paige, *J. Am. Chem. Soc.*, 1966, **88**, 2616; G. E. Hartzell and J. N. Paige, *J. Org. Chem.*, 1967, **32**, 459; K. Kondo, M. Matsumoto, and A. Negishi, *Tetrahedron Lett.*, 1972, 2131; P. Chao and D. M. Lemal, *J. Am. Chem. Soc.*, 1973, **95**, 920; D. M. Lemal and P. Chao, *J. Am. Chem. Soc.*, 1973, **95**, 922; W. G. L. Aalbersberg and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, 1977, **99**, 2792; R. S. Glass and W. Jung, *Sulfur Lett.*, 1994, **17**, 183; I. A. Abu-Yousef and D. N. Harpp, *Tetrahedron Lett.*, 1995, **36**, 201; I. A. Abu-Yousef and D. N. Harpp, *J. Org. Chem.*, 1997, **62**, 8366.