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

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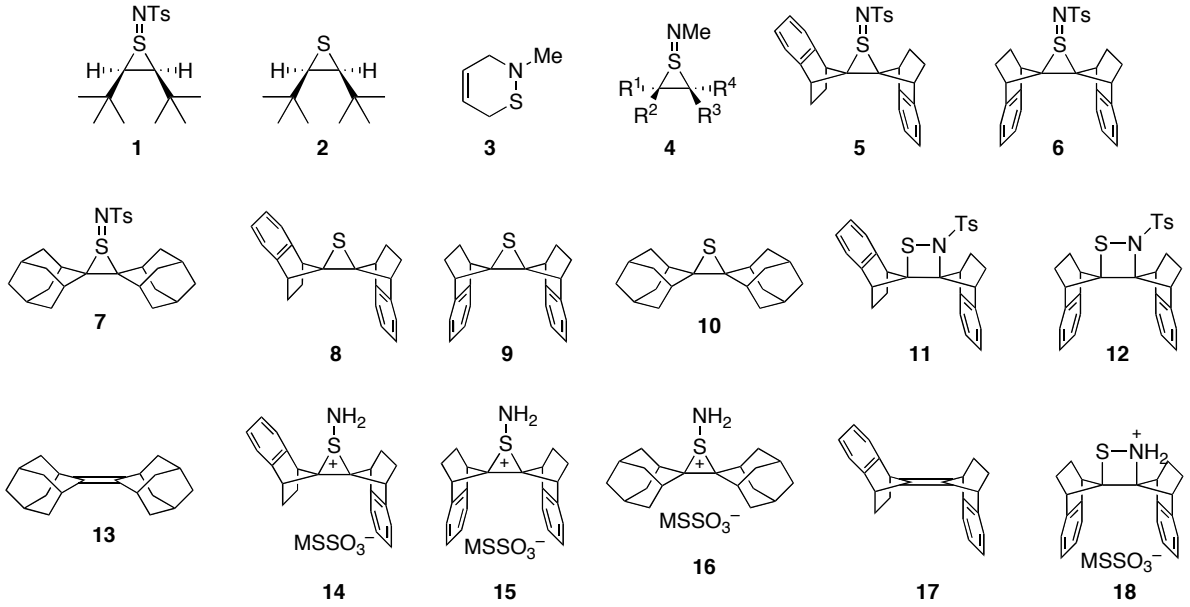
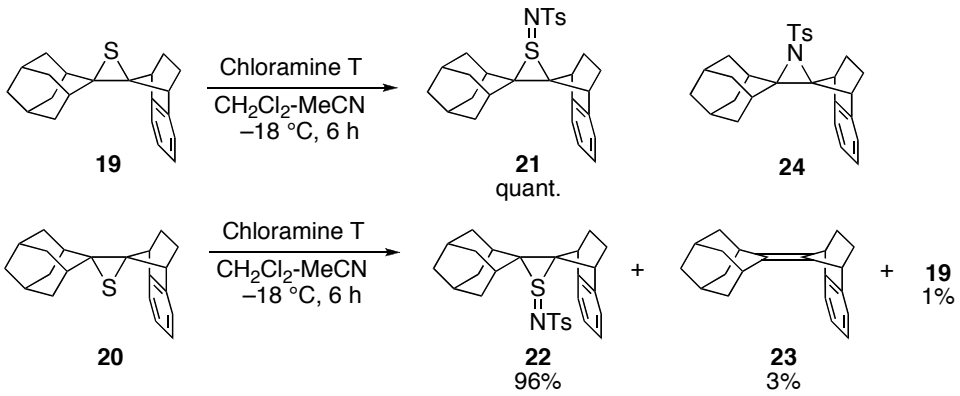
Abstract – Two isolable thiirane 1-imides **21** and **22** were synthesized successfully by imination of *anti*- and *syn*-2'-adamantylidene-9-benzonorbornenylidene sulfides **19** and **20** with Chloramine T in CH_2Cl_2 and MeCN at −18 °C. Thermal decompositions of **21** and **22** in solution at 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.[2–4] 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

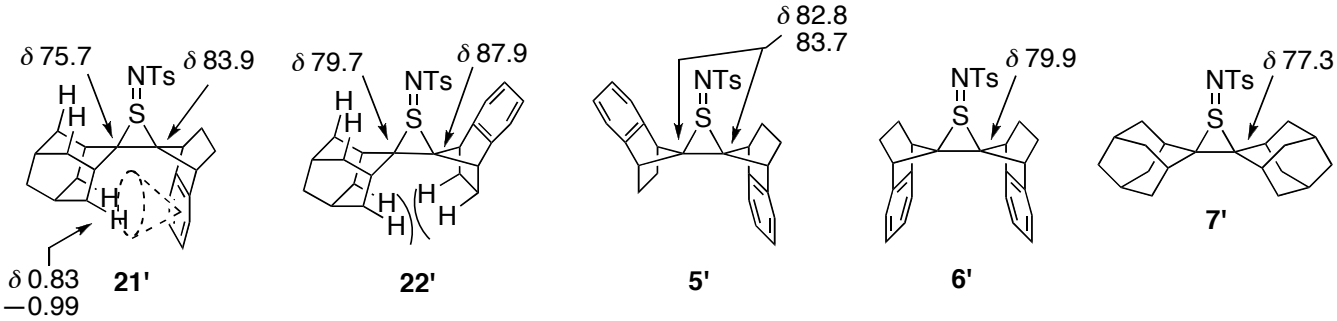
thiiranes.[6] The decomposition products seemed to strongly depend on the substituents connecting with the thiirane ring. Here, we report the synthesis and thermal decomposition of thiirane 1-imides of 2'-adamantylidene-9-benzonorbornenylidene.



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]

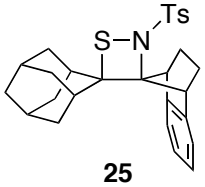


Both **21** and **22** decomposed in solution at room temperature, or in the solid state on heating (Table 1). Thus, allowing a $CDCl_3$ solution of **21** to stand at room temperature for 10 days gave **19**, **23**, and **24** in 36%, 59%, and 5% yields, respectively, and that of **22** afforded **19**, **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**

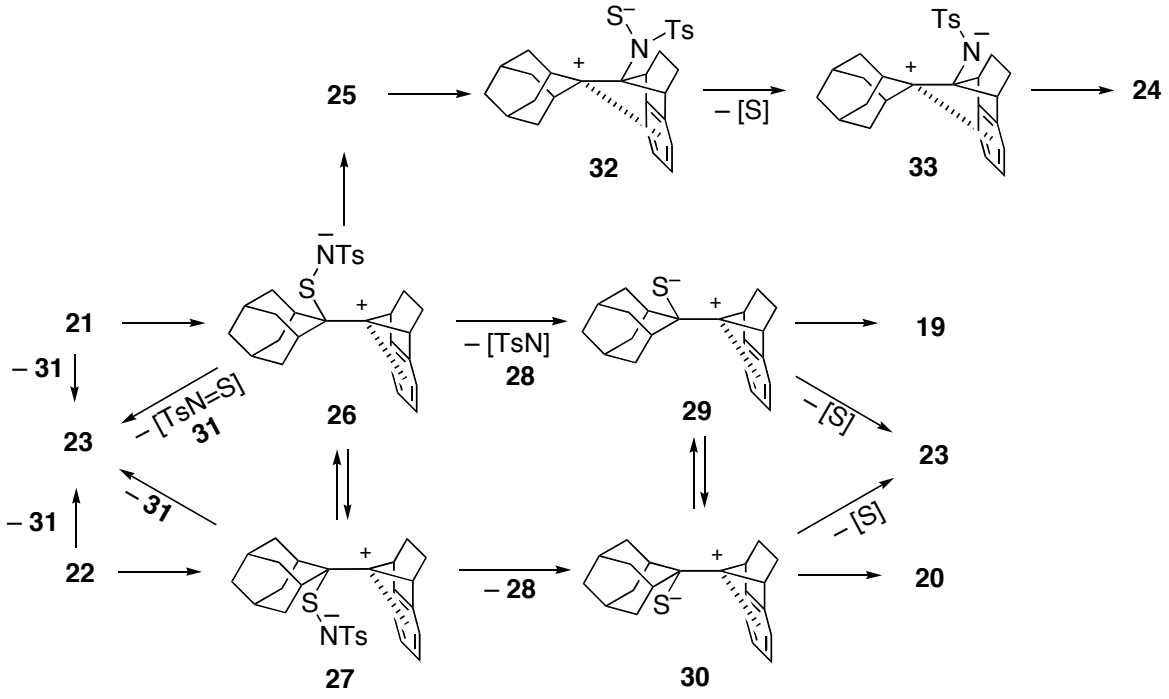
thiirane 1-imide	conditions	yield (%) **19**	**20**	**23**	**24**
21	$CDCl_3$, 25 °C, 10 d	36	—	59	5
22	$CDCl_3$, 25 °C, 10 d	19	2	75	4
21	CD_2Cl_2, 25 °C, 10 d	55	—	37	8
22	CD_2Cl_2, 25 °C, 10 d	50	2	41	7
21	neat, 110 °C, 5 h	55	—	18	27
22	neat, 100 °C, 5 h	43	2	39	16



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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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.

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