Conversions of Thiirene 1-Oxides to α-Iminothioketones or Oxazoles through Probable Intermediates Sulfilimines

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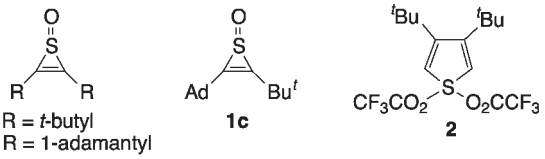
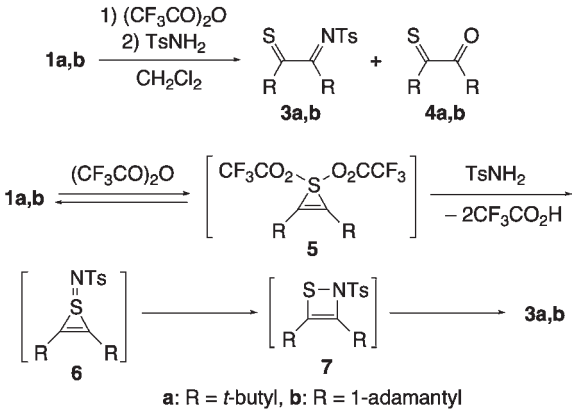
(Received November 8, 2001; CL-011121)

Three thiirene 1-oxides **1**, which possess bulky alkyl substituents at the 2- and 3-positions, afforded α-iminothioketones in 59–69% yields on successive treatment with trifluoroacetic anhydride and *p*-toluenesulfonamide, whereas **1** furnished oxazoles in 65–89% yields on the same treatment with trifluoroacetic anhydride and *p*-toluamide. A mechanism involving ring-expansion of the initial intermediates, sulfilimines, is proposed for these reactions.

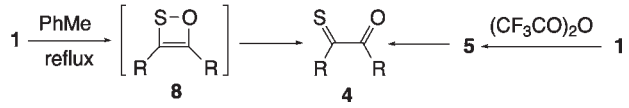
Thiirene 1-oxides, the smallest cyclic and unsaturated sulfoxide, are of much interest in syntheses, structures, and reactions, but their chemistry is still in the development stage.[1–3] Recently, we devised a practical synthesis of thiirene 1-oxides **1a-c** that possess bulky alkyl substituents at the 2- and 3-positions.[4] We have now examined conversions of **1** to the corresponding sulfilimines. This work led us to the finding that the resulting sulfilimines undergo a very quick ring-expansion to produce 1,2-thiazetes.



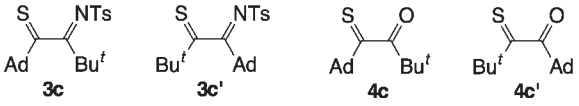
3,4-Di-*t*-butylthiophene 1-oxide and other sulfoxides are satisfactorily converted to the corresponding sulfilimines through intermediates such as **2** by treatment with trifluoroacetic anhydride and then with *p*-toluenesulfonamide.[5,6] Thus, thiirene 1-oxides **1** were treated with these reagents with expectation of obtaining the corresponding sulfilimines **6**, whose synthesis was not hitherto reported. Unexpectedly, however, successive treatment of thiirene 1-oxide **1a** with trifluoroacetic anhydride and *p*-toluenesulfonamide in CH_2Cl_2[7] produced α-iminothioketone **3a**[8] and α-oxothioketone **4a**[4] in 59 and 11% yields, respectively, with recovery of **1a** in 9% yield. Similar treatment of **1b** gave **3b**[9] and **4b**[4] in 66 and 7% yields, respectively, with recovery of **1b** in 10% yield. Expected sulfilimines **6** were not formed even in trace amounts. The formation of **3** can best be explained by assuming i) the initial formation of the sulfilimines **6** through **5**, ii) ring-expansion of **6** to 1,2-thiazetes **7**, and iii) ring-opening of **7** to **3**. Previously, we proposed that the thiazete **7b** tautomerizes to the ring-opened form **3b** exclusively.[9]



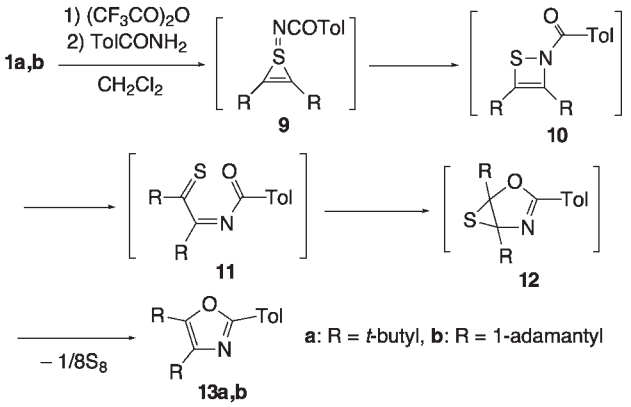
Thiirene 1-oxides are known to isomerize to α-oxothioketones **4** through 1,2-oxathietes **8** when heated.[4] However, this would not be true for the formation of **4** in the present case because, interestingly, treatment of **1a** or **1b** with trifluoroacetic anhydride alone in CH_2Cl_2 produced a nearly quantitative yield of α-oxothioketone **4a** or **4b**, respectively. Therefore, another mechanism probably involving **5** as intermediates seems to be operative for the formation of **4**.



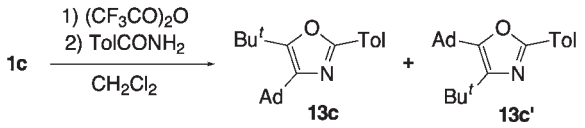
As expected from the mechanisms discussed above, successive treatment of unsymmetrically substituted thiirene 1-oxide **1c** with trifluoroacetic anhydride and *p*-toluenesulfonamide produced 1 : 1 mixtures of **3c** and **3c′**[8] and of **4c** and **4c′**[4] in 69 and 10% yields, respectively, with recovery of **1c** in 10% yield.



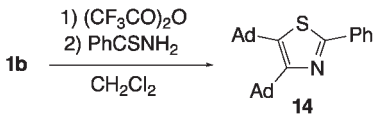
When *p*-toluamide was used in place of *p*-toluenesulfonamide, the reactions provided more unexpected results. Thus, treatment of **1a** and **1b** with trifluoroacetic anhydride and then with *p*-toluamide in CH_2Cl_2 produced oxazoles **13a**[8] and **13b**[8] in 89 and 65% yields, respectively, in addition to elemental sulfur. Also in these cases, 1,2-thiazetes **10** would be formed initially via sulfilimines **9**. Thiazetes **10** then undergo a ring-opening to give **11**. An electrocyclization of **11** would produce thiiranes **12**.[10] Finally, sulfur extrusion of **12** furnishes hetroaromatic oxazoles **13**.



As expected from the mechanism, **1c** produced a 1 : 1 mixture of **13c** and **13c′** in 81% yield by the same treatment.



The use of thiobenzamide, instead of *p*-toluamide, in the reaction of **1b** produced thiazole **14** in 50% yield probably by the same mechanism as that for the formation of **13**.



The reaction reported above would be important not only as a new synthesis of oxazoles (thiazole) but also as a synthesis of oxazoles that possess two bulky alkyl substituents at vicinal positions.[11]

It would be thus concluded that sulfilimines **6** and **9** are more susceptible to ring-opening than the corresponding thiirene 1-oxides, and quickly isomerize to 1,2-thiazetes from which final products are derived.[12]

This work was supported a Grant-in-Aid for Scientific Research in Priority Areas (No. 13029016) from the Ministry of Education, Science, Sports, Culture and Technology.

References and Notes

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7 Thiirene 1-oxide **1a** was dissolved in CH_2Cl_2 containing trifluoroacetic anhydride (2.3 equiv) at −78 °C. After the solution had been stirred for 5 min, *p*-toluenesulfonamide (2.0 equiv) was added. The mixture was stirred for 1 h at −78 °C and then warmed to room temperature. The reaction was quenched by addition of aq. $NaHCO_3$.

8 Satisfactory elemental analyses were obtained for all new compounds. The following are relevant spectroscopic data including mp or bp. **3a**: mp 55–56 °C; purple blocks; ^{1}H NMR ($CDCl_3$) δ 1.24 (9H, s), 1.57 (9H, s), 2.42 (3H, s), 7.29 (2H, d, J = 8.3 Hz), 7.74 (2H, d, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$) δ 21.6, 30.2, 31.8, 42.0, 52.6, 127.2, 129.4, 137.3, 143.7, 194.4, 266.8. A 1 : 1 mixture of **3c** and **3c′**: mp 98–100 °C; purple needles; ^{1}H NMR ($CDCl_3$) δ 1.23 (9H, s), 1.56 (9H, s), 1.60–2.56 (30H, m), 2.42 (6H, s), 7.28 (2H, d, J = 8.6 Hz), 7.29 (2H, d, J = 8.0 Hz), 7.727 (2H, d, J = 8.6 Hz), 7.733 (2H, d, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$) δ 21.6, 27.0, 30.3, 31.6, 31.8, 36.1, 36.2, 36.31, 36.44, 41.9, 42.1, 43.5, 52.6, 55.3, 124.2, 127.1, 129.4, 137.4, 137.5, 143.6, 194.0, 266.1, 266.4. **13a**: bp 130–135 °C/5 mmHg (bulb-to-bulb distillation); colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.42 (9H, s), 1.46 (9H, s), 2.37 (3H, s), 7.20 (2H d, J = 7.9 Hz), 7.85 (2H, d, J = 7.9 Hz); ^{13}C NMR ($CDCl_3$) δ 21.4, 30.9, 31.7, 32.2, 33.0, 125.6, 125.8, 129.2, 139.2, 143.0, 152.4, 155.6; MS m/z 271 (M^+). **13b**: mp 196–197 °C; colorless crystals; ^{1}H NMR ($CDCl_3$) δ 1.78 (12H, m), 2.09 (6H, m), 2.14 (6H, m), 2.17 (6H, m), 2.36 (3H, s), 7.19 (2H, d, J = 8.4 Hz), 7.84 (2H, d, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 21.4, 28.6, 29.0, 34.6, 35.7, 36.7, 36.8, 41.9, 42.9, 125.6, 125.8, 129.1, 139.1, 143.9, 153.5, 155.8; MS m/z 427 (M^+). A 1 : 1 mixture of **13c** and **13c′**: mp 105–106 °C; colorless crystals; ^{1}H NMR ($CDCl_3$) δ 1.43 (9H, s), 1.47 (9H, s), 1.78 (12H, m), 2.08 (12H, m), 2.12 (6H, m), 2.16 (6H, m), 2.37 (6H, s), 7.20 (4H, d, J = 8.3 Hz), 7.84 (4H, d, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$) δ 21.4, 28.6, 28.9, 31.2, 32.0, 32.3, 33.2, 34.5, 35.5, 36.7, 36.8, 41.7, 42.6, 125.6, 125.7, 125.8, 129.2, 139.1, 139.2, 143.2, 143.6, 153.0, 153.1, 155.6, 155.8; MS m/z 349 (M^+). **14**: mp 85–89 °C; colorless solid; ^{1}H NMR ($CDCl_3$) δ 1.77–1.83 (12H, m), 2.11 (6H, br s), 2.25 (6H, d, J = 2.7 Hz), 2.31 (6H, d, J = 2.7 Hz), 7.30–7.39 (3H, m), 7.89 (2H, dd, J = 8.3, 1.6 Hz); ^{13}C NMR ($CDCl_3$) δ 29.2, 29.3, 36.4, 36.9, 37.1, 39.7, 43.5, 45.0, 125.9, 128.6, 128.7, 134.5, 146.1, 158.4, 159.2; MS m/z 349 (M^+).

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12 Attempts to detect sulfilimines or 1,2-thiazetes by ^{1}H NMR were all unsuccessful.