Pergamon

Tetrahedron Letters 42 (2001) 3117–3119

TETRAHEDRON
LETTERS

An *S*-oxide of 6-*tert*-butyl-6-phenylpentathiane. Structure in the crystalline state and in solution and thermal decomposition

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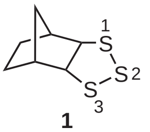
Received 25 December 2000; revised 8 February 2001; accepted 2 March 2001

Abstract—Oxidation of 6-*tert*-butyl-6-phenylpentathiane with trifluoroperacetic acid gave the pentathiane 3-oxide mainly as the monooxide. The 3-oxide takes a twist conformation both in the crystalline state and in solution. Thermal decomposition of the 3-oxide in the presence of 2,3-dimethyl-1,3-butadiene yielded both S_2O- and S_2-transferred products. © 2001 Elsevier Science Ltd. All rights reserved.

Oxidation of cyclic polysulfides has been drawing much attention not only for the fundamental interest in the regio- and stereochemistries[1–4] but also for the potential of the resulting oxides as a precursor of reactive sulfur species.[2,4] It has been reported that oxidation of cyclic trisulfides **1**[2] and **2**[3] with MCPBA took place at the 1 and 2 positions with low regioselectivity, which is in contrast to the highly regioselective MCPBA-oxidation of acyclic tri- and tetrasulfides.[5] Recently, we disclosed that oxidation of 5-(1-adamantyl)-5-*tert*-butyltetrathiolane with dimethyldioxirane took place first at the 2-position and then at the 3-position to give the 2,3-dioxide **3**.[4] The 2,3-dioxide **3** is isolable as crystals at room temperature but decomposed to the dithiirane 1-oxide **4** and S_2O in solution at temperatures higher than −10°C. This result prompted us to investigate oxidation of a higher analog of tetrathiolane, pentathiane **5**.[6]



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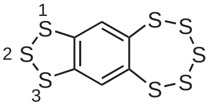

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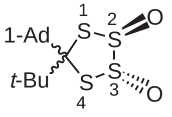

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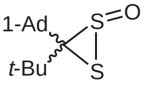

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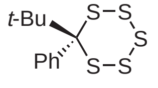
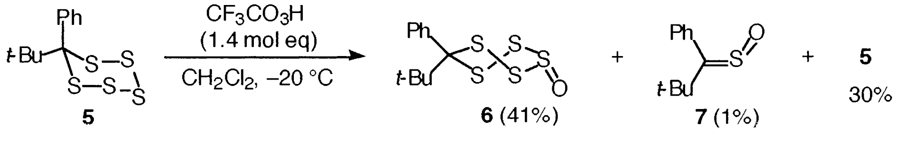


5

Pentathiane **5**[6,7] was oxidized with CF_3CO_3H, prepared in situ from $(CF_3CO)_2O$ (5.3 molar equiv.) and H_2O_2 (1.4 molar equiv.), in CH_2Cl_2 at −20°C. The ^1H NMR integral ratio of the mixture showed the formation of monooxide **6** in 41% yield along with unreacted **5** (30%), thioketone *S*-oxide **7** (1%), and several unidentified compounds. This indicates that **6** was formed at least in 58% yield based on the consumed pentathiane **5**. On a preparative scale, **5** was oxidized with 2 molar equiv. of CF_3CO_3H and, after having been evaporated to dryness, the mixture was washed with hexane, and then recrystallized from hexane–CH_2Cl_2 to give **6** in 25% isolated yield.[8] The monooxide **6** was fairly stable at room temperature. The structure of **6** was finally established by X-ray crystallography to be the 3-oxide, which takes a twist conformation with the oxygen atom *cis* to the *tert*-butyl group (Fig. 1). Meanwhile, the starting pentathiane **5** takes a chair conformation in the crystalline state.[9] The structure of S_6O was reported to take a chair conformation with the oxygen atom occupying the axial position.[10]

Conformations of **5** and **6** in solution (CD_2Cl_2) were investigated by low-temperature ^1H NMR spectroscopy. The singlet (*δ* 1.07) of the *tert*-butyl group of



Keywords: pentathiane; pentathiane 3-oxide; oxidation; structure; thermolysis.

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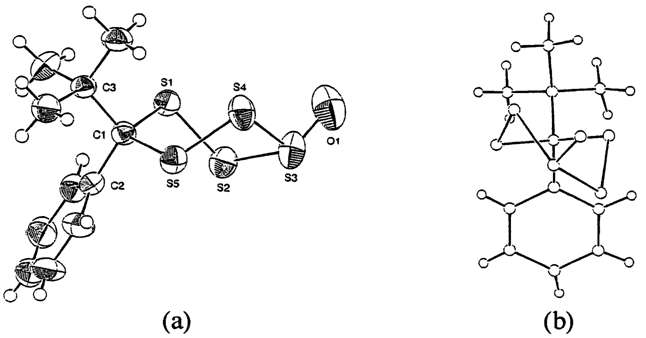
PII: S0040-4039(01)00383-5



(a) (b)

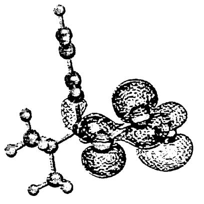
Figure 1. (a) ORTEP drawing of the 3-oxide **6** (50% ellipsoidal probability) and (b) the molecular structure viewed from another direction.

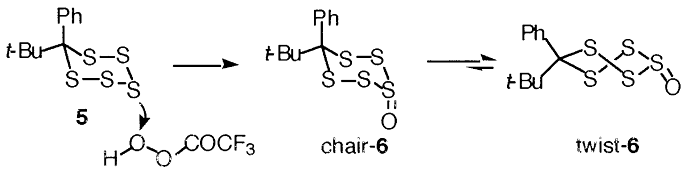
pentathiane **5** decoalesced at temperatures lower than 207 K and changed to two singlets at δ 0.87 (6H) and 1.47 (3H) at 183 K. At low temperatures down to 183 K, the aromatic protons of **5** appeared as measured at room temperature [δ 7.48 (t, 1H), 7.56 (t, 2H), and 7.66 (d, 2H)]. These observations are consistent with the chair conformation of **5** with a mirror plane (C_S symmetry). The ring inversion of the unsubstituted pentathiane at high temperatures has been reported.[11]

On the other hand, the *tert*-butyl group of **6** decoalesced at temperatures lower than 195 K to become two broad singlets at δ 1.05 (6H) and 1.63 (3H), and the five aromatic protons[8] appeared at δ 7.16 (br s, 1H), 7.40 (m, 3H), and 7.81 (d, 1H) at 183 K. The latter indicates the nonequivalency of the aromatic protons to each other. Assuming that two methyls of the *tert*-butyl overlapped at δ 1.05, these observations are in harmony with the twist conformation of **6** [C_1 symmetry, see Fig. 1(b)]. When measured in toluene-d_8 at 183 K, the *tert*-butyl appeared at δ 0.48 (br s, 6H) and 1.18 (br s, 3H), and the aromatic protons at δ 6.44 (m, 1H), 6.65 (m, 1H), 6.76 (m, 2H), and 7.23 (m, 1H).

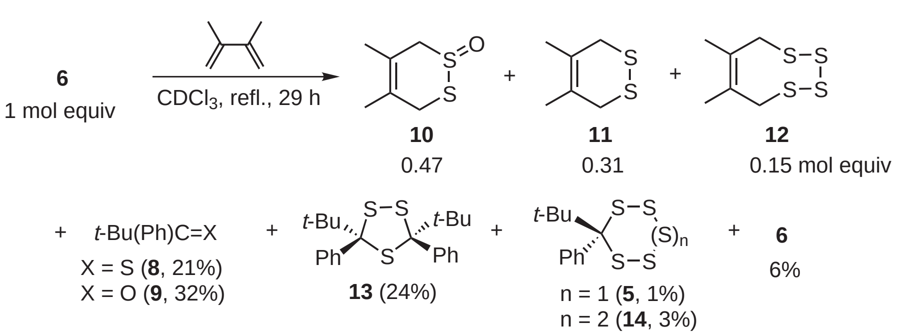
Calculations[12] on **6** at the B3LYP/6-31G* level including solvent effects (the IPCM model[13]) showed that a twist form of **6** (twist-**6**) is more stable than a chair form of **6** (chair-**6**) in CH_2Cl_2 (ε 9.08) and toluene (ε 2.39) by 0.668 and 0.194 kcal mol^{-1}, respectively, whereas the twist-**6** is less stable than the chair-**6** by 0.264 kcal mol^{-1} in the gas phase.[14] Calculated dipole moments of twist-**6** and chair-**6** in CH_2Cl_2 were 6.5577 and 4.4009, respectively. It is reasonable that twist-**6** with a larger dipole moment is more favorable in solution than chair-**6**. Incidentally, a chair form of **5** is 5.9 and 4.4 kcal mol^{-1} more stable than a twist form of **5** in the gas phase and in CH_2Cl_2, respectively, at the B3LYP/6-31G* level.

The stereochemistry **6** shows that the electrophilic attack of CF_3CO_3H took place mainly at the least hindered 3-position from the axial side of a chair form of **5** to give chair-**6**, followed by a conformation change to twist-**6**. At the 3-position of **5**, a molecular orbital derived from lone pair electrons of the sulfur atoms, which is the HOMO at the B3LYP/6-31G* level, spreads in larger extent to the *tert*-butyl side than the phenyl side as depicted at the lower left, supporting the present stereoselectivity.





Pentathiane 3-oxide **6** gradually decomposed in solution at room temperature to give the corresponding thioketone **8** and ketone **9**. The thermal decomposition of **6** in the presence of 2,3-dimethyl-1,3-butadiene yielded three products **10**–**12** along with thioketone **8** and its derivatives, **5**, **9**, **13**, and **14**, where yields of the products were determined by using an internal standard. The formation of **10** indicates the generation of



S_2O,[4,15] while dihydrodithiin **11** and tetrasulfide **12** are known as the products of the reaction of the butadiene and S_2-transfer reagents.[16] Thus, **6** might transfer both S_2O and S_2 to 1,3-butadienes.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research (No. 90193242) from the Ministry of Education, Science, Sports and Culture, Japan.

References

1. Milligan, B.; Swan, J. M. *J. Chem. Soc.* **1965**, 2901–2904.
2. Ghosh, T.; Bartlett, P. D. *J. Am. Chem. Soc.* **1988**, *110*, 7499–7506.
3. (a) Kimura, T.; Hanzawa, M.; Horn, E.; Kawai, Y.; Ogawa, S.; Sato, R. *Tetrahedron Lett.* **1997**, *38*, 1607–1610; (b) Kimura, T.; Kawai, Y.; Ogawa, S.; Sato, R. *Chem. Lett.* **1999**, 1305–1306.
4. Ishii, A.; Nakabayashi, M.; Nakayama, J. *J. Am. Chem. Soc.* **1999**, *121*, 7959–7960.
5. (a) Derbesy, G.; Harpp, D. N. *Sulfur Lett.* **1995**, *19*, 1–10; (b) See also: Derbesy, G.; Harpp, D. N. *Sulfur Reports* **1995**, *16*, 363–369.
6. Jin, Y.-N.; Ishii, A.; Sugihara, Y.; Nakayama, J. *Heterocycles* **1997**, *44*, 255–262.
7. Pentathiane **5** was prepared by the reaction of *t*-Bu(Ph)C=S (**8**) with elemental sulfur in *N*,*N'*-dimethyl-1,3-imidazolidinone at room temperature. The reaction gave **5** and 7-*tert*-butyl-7-phenylhexathiepane (**14**) in improved yields along with *cis*-3,5-di-*tert*-butyl-3,5-diphenyl-1,2,4-trithiolane (**13**). Crystal data for **5**: orthorhombic, $P2_1nb$, $a=12.363(3)$, $b=16.838(4)$, $c=6.607(1)$ Å, $V=1375.3(5)$ Å^3, $Z=4$, $\rho_{\mathrm{calcd}}=1.480$ g cm^{-3}, μ(CuKα) = 74.36 mm^{-1}. Absorption correction was done by the psi-scan method. All independent reflections (1,364) were used for refinement (191 parameters). The final R (R_w) = 0.035 (0.047) and GOF = 1.907; max/min residual electron density = 0.23/−0.45 e Å^{-3}. The structure of **13** was also determined by X-ray crystallography, which will be reported elsewhere.
8. Compound **6**: mp 95–96°C (hexane–CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, 283 K): δ 1.25 (s, 9H), 7.30–7.38 (m, 3H) 7.42–7.50 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 283 K): δ 27.0, 43.6, 84.7, 127.6, 128.1, 130.9, 136.8; IR (KBr) 1094 cm^{-1} (S=O). Anal. calcd for $C_{11}H_{14}OS_5$: C, 40.96; H, 4.37. Found: C, 40.08; H, 4.31 (contamination with a small amount of elemental sulfur caused the unsatisfactory result). Crystal data for **6**: monoclinic, $P2_1/c$, $a=10.290(1)$, $b=20.718(2)$, $c=6.6140(5)$ Å, $\beta=93.555(4)$°, $V=1407.3(2)$ Å^3, $Z=4$, $\rho_{\mathrm{calcd}}=1.522$ g cm^{-3}, $F(000)=672$, μ(MoKα) = 0.80 mm^{-1}. A yellow plate with dimensions 0.30×0.16×0.06 mm was mounted on a Mac Science DIP3000 diffractometer with a graphite-monochromater. The data reduction was made by the maXus program system; 2871 unique reflections; 1915 reflections [$I \geq 2\sigma(I)$] were used for refinement (210 parameters). The final $R_1=0.049$, $wR_2=0.064$, and GOF = 1.585; max./min. residual electron density = 0.72/−0.38 e Å^{-3}. Selected bond lengths (Å) and angles (°): C1–S1, 1.845(3); S1–S2, 2.008(1); S2–S3, 2.182(1); S3–S4, 2.157(2); S4–S5, 1.999(1); S5–C1, 1.887(3); C1–C2, 1.525(4); C1–C3, 1.585(4); S3–O1, 1.432(4); S2–S1–C1, 102.8(2); S1–S2–S3, 104.7(1); S2–S3–S4, 96.9(1); S2–S3–O1, 113.2(2); S4–S3–O1, 102.7(2); S3–S4–S5, 103.8(1); S4–S5–C1, 105.7(2), S1–C1–S5, 107.6(2), C2–C1–C3, 113.3(3).
9. Fehér, F.; Lex, J. Z. *Anorg. Allg. Chem.* **1976**, *423*, 103–111.
10. Steudel, R.; Steidel, J. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 134–135.
11. (a) Fehér, F.; Degen, B.; Söhngen, B. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 301; (b) See also: Allinger, N. L.; Hickely, M. J.; Kao, J. *J. Am. Chem. Soc.* **1976**, *98*, 2741–2745.
12. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, Jr., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.
13. Foresman, J. B.; Keith, T. A.; Wiberg, K. B.; Snoonian, J.; Frisch, M. J. *J. Phys. Chem.* **1996**, *100*, 16098–16104.
14. At the MP2/6-31G* level, chair-**6** is more stable than twist-**6** both in the gas phase (1.35 kcal mol^{-1}) and in CH_2Cl_2 (0.207 kcal mol^{-1}).
15. Dodson, R. M.; Srinivasan, V.; Sharma, K. S.; Sauers, R. F. *J. Org. Chem.* **1972**, *37*, 2367–2372.
16. For a review, see: Steliou, K. *Acc. Chem. Rev.* **1991**, *24*, 341–350. For more recent papers, see: (a) Tardif, S. L.; Rys, A. Z.; Abrams, C. B.; Abu-Yousef, I. A.; Lesté-Lasserre, P. B. F.; Schultz, E. K. V.; Harpp, D. N. *Tetrahedron* **1997**, *53*, 12225–12236; (b) Rys, A. Z.; Harpp, D. N. *Tetrahedron Lett.* **1998**, *39*, 9139–9142; (c) Abu-Yousef, I. A.; Harpp, D. N. *J. Org. Chem.* **1998**, *63*, 8654–8660; (d) Lesté-Lasserre, P.; Harpp, D. N. *Tetrahedron Lett.* **1999**, *40*, 7961–7964; (e) Sawayama, A. M.; Leste-Lasserre, P.; Harpp, D. N. *Sulfur Lett.* **2000**, *23*, 163–168.