Pergamon

Tetrahedron Letters, Vol. 38, No. 14, pp. 2501-2504, 1997

0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)00377-8

The First Isolation of a Telluroketone and Its Reversible Dimerization

Mao Minoura,[1] Takayuki Kawashima, and Renji Okazaki*

Department of Chemistry, Graduate School of Science, The University of Tokyo,
7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

Abstract: The solid-state thermolysis of a sterically hindered Δ^3-1,3,4-telluradiazoline **2** afforded products resulting from intermediary tellone **1** and diazo compound **8** formed by retrocyclization, whereas the flash vacuum thermolysis of **2** led to isolation of tellone **1** as green needles. The spontaneous dimerization of **1** thus obtained occurred in the solid state to give the corresponding 1,3-ditelluretane **10**, which underwent the thermal cycloreversion in solution to regenerate pure tellone **1**.

Compounds containing a carbon-tellurium double bond are known to be unstable. The most prevalent way to stabilize a C=Te bond is the introduction of heteroatom substituents on the tellurocarbonyl carbon, and some heteroatom stabilized tellurocarbonyl compounds have been reported[2] since the first synthesis of telluroesters by Barton et al. in 1979.[3] In contrast to well known thio-[4] and selenoketones,[5] telluroketones (tellones) without such electronic stabilization have proved elusive because of the weakness of a C_{2p}-Te_{5p} π bonding and the lack of suitable synthetic methods, although some transient tellones[6] and their cyclic dimers have been reported.[6, 7] We have recently communicated the synthesis of tellone **1** stable in solution by use of thermal cycloreversion of 1,3,4-telluradiazoline **2**[8] and the isolation of $^1\eta$-complex of **1** which regenerates **1** upon heating in acetonitrile.[9]

We report here the flash vacuum thermolysis of 1,3,4-telluradiazoline **2** leading to the isolation of tellone **1** as green crystals and its solid-state dimerization to the corresponding 1,3-ditelluretane which can reproduce pure tellone **1** upon thermolysis in solution.[10]

The solid state thermolysis of **2**[11] was performed at 80, 160 and 200 °C for 6 h in sealed tubes. Although **2** was stable at 80 °C for 6 h without any perceptible decomposition, pyrolysis at 160 and 200 °C afforded decomposition products **3** – **7** (Scheme 1 and Table1). On the contrary, thermolysis of the corresponding selenadiazoline **9** under similar conditions (190 °C, 24 h) gave a mainly a two fold extrusion product **3** (70%).[12]

Scheme 1.

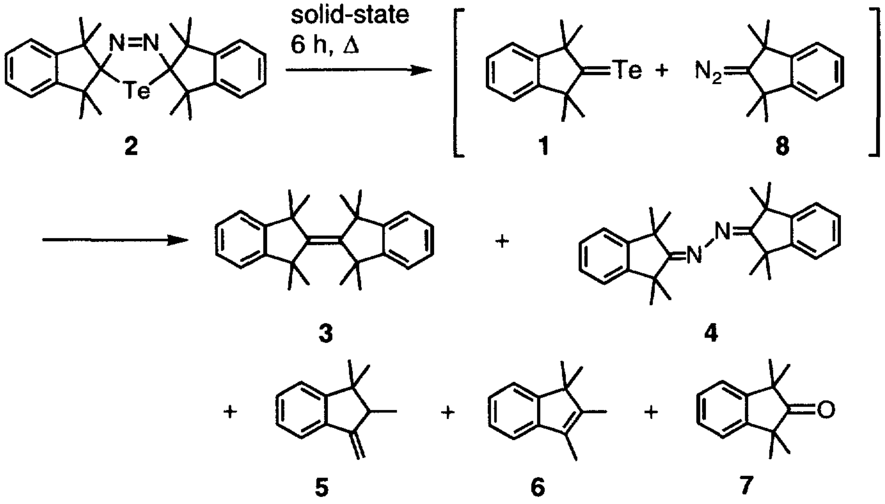


Table 1. Reaction Products of the Thermolysis of **2**[a]

	Yield / %				
	3	**4**	**5**	**6**	**7**
80 °C			no reaction		
160 °C	27	13	43	108	9
200 °C	15	8	29	144	4

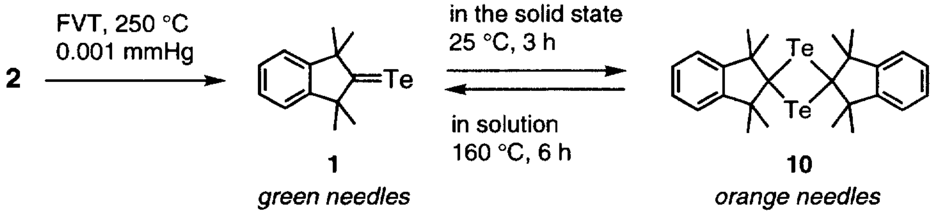
a: The product distribution was determined by integrating the peak area (2.1 — 0.9 ppm) of methyl groups in the ^{1}H NMR ($CDCl_3$).

The relatively low yield of the two fold extrusion product **3** in the reaction of **2** compared with the thermolysis of **9** seems to be due to competitive reaction leading to tellone **1** and the diazo compound **8**, which was observed in the thermolysis in solution,[8] followed by the decomposition of **1** and **8** giving **5**, **6**, and **7**. These results prompted us to attempt the isolation of **1** using the flash vacuum thermolysis (FVT) technique.[13]

The FVT of **2** was carried out at 250 °C under the pressure of 1×10^{-3} mmHg. Vapor of **2**, which was generated by heating solid **2** mixed well with quartz sand at 200 °C, was passed through a quartz tubing (60 cm long, 2 cm in diameter). Green solid products containing **1**, **5**, and **6** were collected in the cold trap at -78 °C during 3 h, while **3** and **4** remained in the quartz sand along with unchanged **2**. Heating the green solid products in the first cold trap under reduced pressure vaporized **1**, **5**, and **6**, among which **1** was trapped in the second cold trap at -78 °C whereas **5** and **6** were trapped at the third trap cooled by liquid nitrogen. Tellone **1** thus purified is an emerald green crystalline compound. The NMR and electronic spectra of the green needles taken in a sealed NMR tube ($CDCl_3$) and in a sealed UV-vis cell ($CHCl_3$), respectively, were identical with those taken for **1** obtained from the thermolysis of **2** in solution.[8]

Interestingly, the green color of the crystalline tellone **1** gradually faded away within several hours at room temperature and orange crystalline 1,3-ditelluretane **10** was formed quantitatively (Scheme 2). The head-to-tail structure of the tellone dimer **10** was characterized by spectroscopic means.[14] The dimer **10** is stable toward oxygen, water, and light, and the yield of **1** isolated in the FVT was estimated to be ca. 40% on the basis of the yield of **10**.

Scheme 2.



Although **10** was stable in the solid state, it slowly decomposed in solution contaminated with oxygen. Dissociation of **10** into **1** proceeded in an absolutely deaerated $CDCl_3$ solution at 160 °C in a sealed tube over 6 h. Intermittent monitoring by ^1H NMR revealed the quantitative formation of **1**; the signals of **10** were decreased with concomitant increase of the signals due to **1**. Tellone **1** was thermally quite stable,[8] surviving after heating at 160 °C for 6 h and standing for as long as a few days at room temperature. Interestingly, any dimerization product was not observed in solution.

Acknowledgement: This work was supported by a Grant-in-Aid for Scientific Research No. 04403005 from the Ministry of Education, Science and Culture, Japan.

REFERENCES AND NOTES

1. Present address: Hiroshima University, Department of Chemistry, Faculty of Science, 1-3-1 Kagamiyama, Higashi-Hiroshima 739, Japan.
2. Barrett, A. G. M.; Barton, D. H. R.; Read, R. W. *J. Chem. Soc., Chem. Commun.* **1979**, 645-647.
3. Grshovich, M. Z.; Elitsov, A. V. *Z. Obshch. Khim.* **1969**, *39*, 941-942; Lerstrup, K. A.; Henriksen, L. *J. Chem. Soc., Chem. Commun.* **1979**, 1102-1103; Lappert, M. F.; Martin, T. R.; McLaughlin, G. M. *J. Chem. Soc., Chem. Commun.* **1980**, 635-637; Barrett, A. G. M.; Read, R. W.; Barton, D. H. R. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2191-2195; Severengiz, T.; du Mont, W. W. *J. Chem. Soc., Chem. Commun.* **1987**, 820-821; Kato, S.; Kageyama, H.; Kanda, T.; Murai, T.; Kawamura, T. *Tetrahedron Lett.* **1990**, *31*, 3587-3590; Segi, M.; Kojima, A.; Nakajima, T.; Suga, S. *Synlett* **1991**, *2*, 105-106. Kuhn, N.; Henkel, G.; Kratz, T. *Chem. Ber.* **1993**, *126*, 2047-2049; Kawahara, Y.; Kato, S.; Kanda, T.; Murai, T.; Ebihara, M. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 3507-3517; Kato, S.; Kawahara, Y.; Kageyama, H., Yamada, R.; Niyomura, O.; Murai, T.; Kanda, T. *J. Am. Chem. Soc.* **1996**, *118*, 1262-1267.
4. Duss, F. In *Comprehensive Organic Chemistry*; Barton, D. H. R.; Ollis, W. D., Eds.; Pergamon: Oxford, 1979; Vol. 3, pp 373-487; Voss, J. In *Houben-Weyl Methoden der Organischen Chemie*; Klamann, D. Ed.: George Thieme: New York, 1985; Bd. E11, pp 188-231.

5. Magnas, P. D. In *Comprehensive Organic Chemistry*; Barton, D. H. R.; Ollis, W. D., Eds.; Pergamon: Oxford, 1979; Vol. 3, pp 491-538; Paulmier, C. *Selenium Reagents and Intermediates in Organic Synthesis*; Pergamon: Oxford, 1986; pp 58-83; Guziec, F. S., Jr. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S. Ed.; John Wiley & Sons: New York, 1987; Vol. 2, pp 215-273; Guziec, F. S. Jr.; Guziec, L. J. In *Comprehensive Organic Functional Group Transformations*; Pattenden, G., Ed.; Katritzky, A. R.; Meth-Cohn, O., Rees, C. W., Eds.-in-Chief; Pergamon: Oxford, 1995; Vol. 3, pp 381-401.
6. Segi, M.; Koyama, T.; Takata, Y.; Nakajima, T.; Suga, S. *J. Am. Chem. Soc.* **1989**, *111*, 8749-8751; Back, T. G.; Dyck, B. P.; Parvez, M. *J. Org. Chem.* **1995**, *60*, 4657-4659; also see: Erker, G.; Hock, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 179-180.
7. Boese, R.; Haas, A.; Limberg, C. *J. Chem. Soc., Chem. Commun.* **1991**, 1378-1379; Boese, R.; Haas, A.; Limberg, C. *J. Chem. Soc., Dalton Trans.* **1993**, 2547-2556. Beck, J.; Haas, A.; Herrendorf, W.; Heuduk, H. *J. Chem. Soc., Dalton Trans.* **1996**, 4463-4470. For other examples of 1,3-ditelluretanes see: Laishev, V. Z.; Petrov, M. L.; Petrov, A. A. *Z. Org. Kim.* **1981**, *17*, 2064-2071; Bender, S. L.; Haley, N. F.; Luss, H. R. *Tetrahedron Lett.* **1981**, *22*, 1495-1496; Lakshmikantham, M. V.; Cava, M. P.; Albeck, M.; Engman, L.; Carroll, P.; Bergman, J.; Wudl, F. *Tetrahedraon Lett.* **1981**, *22*, 4199-4200.
8. Minoura, M.; Kawashima, T.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, *115*, 7019-7020.
9. Minoura, M.; Kawashima, T.; Tokitoh, N.; Okazaki, R. *J. Chem. Soc., Chem. Commun.* **1996**, 123-124.
10. In these experiments, all manipulations were performed in the dark with a subdued red lump except for cases of checking the color.
11. Okazaki, R.; Minoura, M.; Kawashima, T. *Chem. Lett.* **1993**, 1047-1048.
12. Guziec, F. S., Jr.; SanFilippo, L. J.; Murphy, C. J.; Moustakis, C. A.; Cullen, E. R. *Tetrahedron* **1985**, *41*, 4843-4852. Also see followings. Back, T. G.; Barton, D. H. R.; Britten-Kelly, M. R.; Guziec, F. S., Jr. *J. Chem. Soc., Perkin Trans. 1* **1976**, 2079-2089; Guziec, F. S., Jr; Murphy, C. J.; Cullen, E. R. *J. Chem. Soc., Perkin Trans. 1* **1985**, 107-113.
13. Wiersum, U. E. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 317-332, 365-381.
14. 1,1,1",1",3,3,3",3"-Octamethyldispiro[indane-2,2'-[1,3]ditelluretane-5',2"-indane] (**10**): Orange needles; mp 189-190 °C (decomp); ^{1}H NMR(CDCl$_3$, 500 MHz) $\delta = 1.79$(s, 24H), 7.17(s, 8H); ^{13}C NMR(CDCl$_3$, 125 MHz) $\delta = 10.0$(s), 34.8(q), 50.4(s), 123.0(d), 127.2(d), 146.7(s); ^{125}Te NMR(CDCl$_3$, 85.1 MHz) $\delta = 977.9$; UV-vis(CHCl$_3$) λ_{max} 519 nm (ε 92). HRMS (FAB) Found: *m/z* 600.0604: Calcd for $C_{26}H_{32}{}^{128}Te_2$: M, 600.0594.

(*Received in Japan* 27 *January* 1997; *revised* 20 *February* 1997; *accepted* 21 *February* 1997)