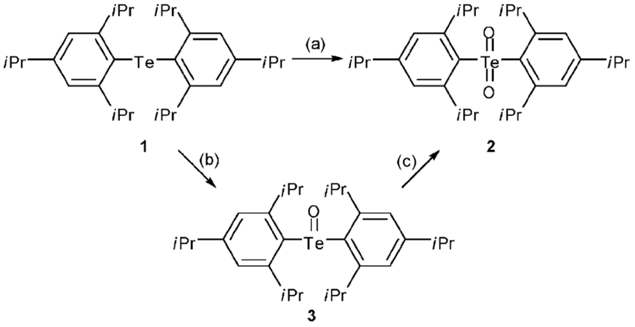
Synthesis, characterization and oxidizing properties of a diorgano tellurone carrying bulky aromatic substituents†

Makoto Oba,[a] Yasunori Okada,[a] Kozaburo Nishiyama,*[a] Shigeru Shimada[b] and Wataru Ando*[b]

Received (in Cambridge, UK) 30th June 2008, Accepted 7th August 2008
First published as an Advance Article on the web 17th September 2008
DOI: 10.1039/b811112j

Bis(2,4,6-triisopropylphenyl) tellurone (Tip_2TeO_2) was prepared, fully characterized by spectroscopic and X-ray crystallographic analyses, as well as theoretical calculations, and found to be an effective oxidizing agent that was capable of converting alcohols into carbonyl compounds under mild reaction conditions.

Diorgano tellurones (R_2TeO_2), the tellurium analogues of sulfones, are a novel class of organochalcogen oxides that have not yet been fully characterized. Since 1920, few attempts have been made to prepare tellurones by the oxidation of diorgano tellurides with hydrogen peroxide,[1] which probably resulted in the formation of the hydrogen peroxide adducts of the telluroxides.[2] In 1982, Engman and Cava reported the preparation of bis(4-methoxyphenyl) tellurone, which gave satisfactory analytical data for the first time, by periodate oxidation of the corresponding telluroxide.[3] More recently, a similar approach towards diorgano tellurones, using sodium hypochlorite as an oxidant, was reported by Khurana and coworkers.[4] However, considering the highly polarizable nature of the tellurium–oxygen bond, it is doubtful whether the reported tellurones were obtained in a monomeric form. We prepared bis(4-methoxyphenyl) tellurone according to Cava's procedure, and the product was analyzed by NMR spectroscopy. The ^{1}H, ^{13}C and ^{125}Te NMR spectra exhibited all the characteristics of oligomeric compounds, with extremely broad ^{1}H signals, and many ^{13}C and ^{125}Te signals being observed, despite the compound's highly symmetrical structure. These findings led us to speculate that we were dealing with an oligomeric mixture of the telluroxane type. It is reasonable to expect that bulky substituents placed on the tellurium atom would force the tellurone to retain its monomeric form. In this Communication, we report the synthesis and the first crystal structure of a diorgano tellurone. The bulky diaryl tellurone obtained in this work is also the first chalcogen oxide capable of oxidizing alcohols to their corresponding carbonyl compounds.



Scheme 1 Synthesis of Tip_2TeO_2 (**2**). *Reagents and conditions:* (a) $NaIO_4$ (2.25 equiv.), EtOH–H_2O, 98%; (b) $NaIO_4$ (1 equiv.), EtOH–H_2O, 83%; (c) as in (b), 90%.

When a solution of bis(2,4,6-triisopropylphenyl) telluride (Tip_2Te, **1**) in ethanol was treated with an aqueous solution of sodium periodate (2.25 equiv.) at room temperature overnight, bis(2,4,6-triisopropylphenyl) tellurone (Tip_2TeO_2, **2**) was isolated in 98% yield by precipitation from water (Scheme 1). Tellurone **2** could be also obtained *via* the corresponding telluroxide, **3** (Tip_2TeO), in a stepwise manner. The use of other oxidizing agents, such as hypochlorite, hydrogen peroxide and *meta*-chloroperbenzoic acid, resulted in either a low yield or a complex mixture. Diphenyl telluride and bis(2,4,6-trimethylphenyl) telluride (Mes_2Te) were also subjected to the above oxidation conditions; however, the former gave an oligomeric mixture, as in the case of 4-methoxyphenyl derivative, and the latter afforded only the corresponding telluroxide (Mes_2TeO) in 87% yield.

The structure of **2** was confirmed by ^{1}H, ^{13}C and ^{125}Te NMR, MS and IR spectroscopy, as well as elemental analysis.‡ The ^{125}Te NMR spectrum of **2** revealed a signal at δ 1326, which is shifted slightly downfield from that of the corresponding telluroxide, **3** (δ 1314).[5] The FAB-MS spectrum of **2** showed a parent ion peak at m/z = 569 $(MH)^+$. The IR spectrum of **2** in benzene revealed two absorptions at 835 and 805 cm^{-1}, which are in good agreement with the calculated asymmetrical and symmetrical stretching vibrational frequencies of the O–Te–O group (834 and 799 cm^{-1}, respectively),[6] computed at the B3LYP/6-31G(d) + LANL2DZdp(Te)§ level and scaled by 0.98.[7]

The crystal structure of **2** was established by X-ray crystallography (Fig. 1).¶ The two Te–O distances of 1.801(2) and

---

[a] *Department of Materials Chemistry, Tokai University, 317 Nishino, Numazu, Shizuoka 410-0395, Japan. E-mail: nishiyam@wing.ncc.u-tokai.ac.jp; Fax: +81 55 968 1155; Tel: +81 55 968 1111*
[b] *National Institute of Advanced Industrial Science and Technology, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan. E-mail: wataru.ando@aist.go.jp; Fax: +81 29 861 4511; Tel: +81 29 861 6244*

† Electronic supplementary information (ESI) available: General experimental procedures, and ^{1}H, ^{13}C and ^{125}Te NMR spectra. CCDC 691356. For ESI and crystal data for tellurone **2** in CIF or other electronic format, see DOI: 10.1039/b811112j

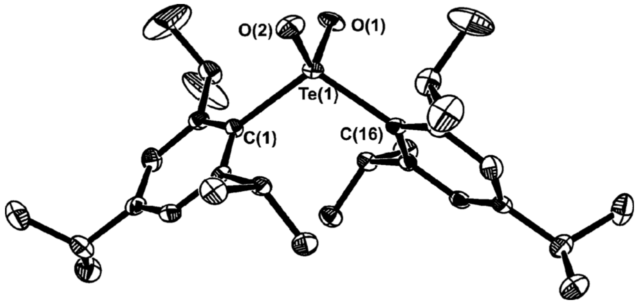


Fig. 1 An ORTEP drawing of Tip_2TeO_2 (**2**), showing 50% probability ellipsoids for the non-hydrogen atoms. Water of crystallization is omitted for clarity. Selected bond lengths (Å) and angles (°): Te(1)–O(1) 1.801(2), Te(1)–O(2) 1.802(3), Te(1)–C(1) 2.127(4), Te(1)–C(16) 2.126(3), O(1)–Te(1)–O(2) 111.17(13), C(1)–Te(1)–C(16) 106.12(15), O(1)–Te(1)–C(1) 114.01(13), O(1)–Te(1)–C(16) 105.58(13), O(2)–Te(1)–C(1) 105.65(15), O(2)–Te(1)–C(16) 114.41(13).

Table 1 Oxidation of alcohols to carbonyl compounds using Tip_2TeO_2 (**2**)

$$\text{alcohol} \xrightarrow[\text{hexane,reflux}]{Tip_2TeO_2\text{(2 equiv.)}} \text{carbonyl compound}$$

Run	Alcohol	Time/h	Product (%)[a]
1[b]	$4\text{-}BrC_6H_4CH_2OH$	8	$4\text{-}BrC_6H_4CHO$ (96)
2	$4\text{-}BrC_6H_4CH_2OH$	1	$4\text{-}BrC_6H_4CHO$ (quant.)
3	$PhCH_2OH$	1	PhCHO (quant.)
4	$4\text{-}MeOC_6H_4CH_2OH$	1	$4\text{-}MeOC_6H_4CHO$ (quant.)
5	$4\text{-}O_2NC_6H_4CH_2OH$	4	$4\text{-}O_2NC_6H_4CHO$ (94)
6	*trans*-$PhCH{=}CHCH_2OH$	1	*trans*-$PhCH{=}CHCHO$ (quant.)
7	*trans*-2-Dodecenol	1	*trans*-2-Dodecen-1-al (quant.)
8	$PhCH_2CH_2CH_2OH$	2	$PhCH_2CH_2CHO$ (quant.)
9	1-Dodecanol	6	1-Dodecanal (97)
10	2-Dodecanol	2	No reaction
11	$PhCHOHCH_3$	4	$PhCOCH_3$ (87)
12	$PhCHOHCO_2Me$	8	$PhCOCO_2Me$ (77)

[a] Determined by ^1H NMR. [b] The reaction was carried out in refluxing pentane (36 °C).

1.802(3) Å are shorter than those found in Ph_2TeO (Te–O 1.871(18) Å)[8] and $(C_6F_5)_2TeO$ (Te–O 1.875(3) Å),[9] which adopt dimeric structures bonded by secondary Te–O interactions (Te–O 2.563(21) and 2.214(2) Å, respectively). The two Te–C distances of 2.127(4) and 2.126(3) Å are comparable to those commonly found in diaryl telluroxides such as $(4\text{-}MeOC_6H_4)_2TeO$ (Te–O 2.126(2) Å).[10] The atoms arranged around the tellurium atom are in the shape of a regular tetrahedron, with angles ranging from 105.58(13) to 114.41(13)°. In the crystal lattice, two Tip_2TeO_2 molecules interact *via* two water molecules, where the two protons in each water molecule are oriented in such a way that they point towards two different oxygen atoms of different tellurones, and two O–Te–O planes are nearly perpendicular (96.7°) to each other. The distance between the tellurone and the water molecules is typical of a weak hydrogen bond, with an average O–O distance of 2.84 Å.

A theoretical calculation[6] on **2** at the B3LYP/6-31G(d) + LANL2DZdp(Te)§ level efficiently reproduced the experimental structure (calculated bond lengths (Å) and angles (°): Te–O 1.787, Te–C 2.165, O–Te–O 116.98, C–Te–C 105.89). The deviation of the observed O–Te–O angle (111.17(13)°) from the calculated value (116.98°) can be attributed to the interaction with the water molecules in the crystal lattice.

Further structural proof for **2** was obtained by the oxidation of triphenylphosphine with 0.5 equiv. of **2** in refluxing $CDCl_3$. The ^{31}P and ^1H NMR spectra of the reaction mixture revealed quantitative formation of triphenylphosphine oxide, along with the complete recovery of Tip_2Te (**1**), suggesting that **2** involves two reactive Te–O bonds.

The most prominent feature of **2** is its alcohol-oxidizing activity.[11] When a pentane solution of 4-bromobenzyl alcohol and 2 equiv. of **2** were heated to reflux (36 °C) for 8 h, 4-bromobenzaldehyde was obtained in 96% yield (Table 1, run 1). A similar reaction in refluxing hexane (69 °C) was completed within 1 h to give a quantitative yield of the aldehyde (run 2). Other alcohols were also employed as substrates, and representative results are listed in Table 1. In order to shorten turnaround times, all reactions were performed in refluxing hexane. Tellurone **2** was highly reactive toward benzylic and allylic alcohols. Therefore, the corresponding aldehydes were obtained in quantitative yields (runs 3, 4, 6 and 7), although 4-nitrobenzyl alcohol required a longer reaction time (run 5). Note that non-activated alcohols, such as 3-phenylpropanol and 1-dodecanol, were found to undergo oxidation to aldehydes with excellent yields (runs 8 and 9). Moderate reactivity was observed in the oxidation of secondary benzylic alcohols, giving acetophenone and methyl phenylglyoxylate in 87 and 77% yields, respectively (runs 11 and 12), whereas non-activated secondary alcohols such as 2-dodecanol were unreactive (run 10).

We have already reported that the corresponding telluroxide, **3**, could oxidize benzylic and allylic alcohols; however, the reaction should be carried out in refluxing xylene (140 °C).[5] In addition, **3** could not oxidize non-activated alcohols, even at a higher temperature, suggesting an enhanced reactivity of **2** in comparison with **3**.

In conclusion, we have prepared and fully characterized the first monomeric diorgano tellurone, **2**, with the help of bulky aromatic substituents. It has also been demonstrated that **2** is highly reactive towards alcohols, giving the corresponding carbonyl compounds in good yields. Further studies are in progress to broaden the potential of **2** as an oxidizing reagent and to elucidate the reason for its increased alcohol-oxidizing competence.

Financial support from Tokai University is gratefully acknowledged by M. O.

Notes and references

‡ Colorless crystals, mp 108–110 °C. ^1H NMR ($CDCl_3$): δ 1.12 (d, J = 7 Hz, 24H), 1.21 (d, J = 7 Hz, 12H), 2.88 (sept, J = 7 Hz, 2H), 4.09 (sept, J = 7 Hz, 4H) and 7.14 (s, 4H). ^{13}C NMR ($CDCl_3$): δ 23.57, 24.26, 32.74, 34.24, 124.79, 137.82 (d satellite, $J_{Te\text{–}C}$ = 81 Hz), 152.19 and 154.87. ^{125}Te NMR ($CDCl_3$): δ 1326. FAB-MS

(m-NBA): m/z = 569 (MH^+). IR (KBr): ν_{max} = 3470 (O–H), 3050 (C–H), 2960 (C–H), 825 (Te–O) and 800 (Te–O) cm^{-1}. IR (benzene): ν_{max} = 2960 (C–H), 835 (Te–O) and 805 (Te–O) cm^{-1}. Anal. calc. for $C_{30}H_{46}O_2Te{\cdot}H_2O$: C, 61.67; H, 8.28. Found: C, 61.82; H, 8.39%.

§ The LANL2DZdp effective core potential basis set was used for Te, while the 6-31G(d) basis set was used for C, H and O. This combination is denoted as 6-31G(d) + LANL2DZdp(Te).

¶ X-Ray data were collected on a Bruker SMART diffractometer. The structure was solved by direct methods (SHELXS-97) and refined with CRYSTALS. Crystallographic data for **2**: $C_{30}H_{46}O_2Te{\cdot}H_2O$, M_r = 584.31, 0.16 × 0.12 × 0.08 mm, monoclinic, $C2/c$ (#15), a = 24.4967(19), b = 16.1761(12), c = 16.3546(12) Å, β = 111.4460(10)°, V = 6032.0(8) $Å^3$, Z = 8, ρ_{calc} = 1.287 g cm^{-3}, μ = 1.012 mm^{-1}, MoK_α (λ = 0.71069 Å), 153(2) K, $2\theta_{max}$ = 56.5°. Of the 18 070 reflections that were collected, 6755 were unique (R_{int} = 0.043). R = 0.0756 (all reflections), $R1$ = 0.0378 [$I > 2\sigma(I)$], w$R2$ = 0.0911 (all reflections), GOF = 1.052, residual electron density between −0.89 and 1.30 $eÅ^3$. CCDC 691356. See the ESI.†

1 R. H. Vernon, *J. Chem. Soc., Trans.*, 1920, 889.

2 (*a*) K. J. Irgolic, in *The Organic Chemistry of Tellurium*, Gordon and Breach, New York, 1974, pp. 196; (*b*) J. Bergman, L. Engman and J. Sidén, in *The Chemistry of Organic Selenium and Tellurium Compounds*, ed. S. Patai and Z. Rappoport, John Wiley & Sons Ltd., Chichester, 1986, vol. **1**, pp. 550.

3 L. Engman and M. P. Cava, *J. Chem. Soc., Chem. Commun.*, 1982, 164.

4 J. M. Khurana, B. M. Kandpal and Y. K. Chauhan, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2003, **178**, 1369.

5 M. Oba, M. Endo, K. Nishiyama, A. Ouchi and W. Ando, *Chem. Commun.*, 2004, 1672.

6 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *GAUSSIAN 03 (Revision D.02)*, Gaussian, Inc., Wallingford, CT, 2004.

7 C. W. Bauschlicher and H. J. Partridge, *J. Chem. Phys.*, 1995, **103**, 1788.

8 N. W. Alcock and W. D. Harrison, *J. Chem. Soc., Dalton Trans.*, 1982, 709.

9 T. M. Klapötke, B. Krumm, P. Mayer, H. Piotrowski and O. P. Ruscitti, *Z. Naturforsch., B: Chem. Sci.*, 2002, **57b**, 145.

10 J. Beckmann, D. Dakternieks, A. Duthie, F. Ribot, M. Schürmann and N. A. Lewcenko, *Organometallics*, 2003, **22**, 3257.

11 A typical experimental procedure for the oxidation of alcohols with tellurone **2** is as follows. A solution of 4-bromobenzyl alcohol (94.1 mg, 0.503 mmol) and **2** (584 mg, 1.03 mmol) in hexane (5 ml) was refluxed for 1 h. ^1H NMR analysis of the concentrated reaction mixture showed the quantitative formation of 4-bromobenzaldehyde. Purification of the product was performed by flash column chromatography on silica gel and elution with hexane afforded 4-bromobenzaldehyde (90.4 mg, 0.489 mmol) in 97% yield. The structure was confirmed by comparison of the obtained ^1H NMR spectrum and GC retention times with those of an authentic sample.