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# 12-Te-5 Pertelluranes from 1,6-Dioxa-6a-tellurapentalenes. Synthesis, Structure, and Reactivity

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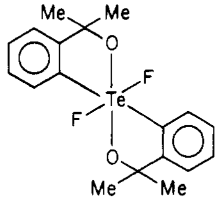
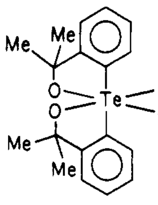
2,5-Diphenyl-1,6-dioxa-6a-tellurapentalene (**6**) is prepared by the condensation of 3-methyl-5-phenyl-1,2-oxatellurolyl-1-ium chloride with benzyl chloride in the presence of triethylamine. The oxidative addition of bromine and chlorine to **6** at low temperature gives 12-Te-5 pertelluranes **7** and **8**. At higher temperatures, **7** and **8** are ring halogenated to give **9** and **10**. The pertelluranes function as mild oxidants for thiols, selenols, and tellurides and are reduced by these reagents and by hydrazine to dioxatellurapentalenes. The structures of **6** and **9** were unambiguously assigned by single-crystal X-ray crystallographic analyses.

Tellurium(VI) compounds have been known in the literature for a number of years,[1] although the first organotellurium(VI) species (**1** and **2**) have been reported only recently.[2] These latter compounds are of the 12-Te-6 class[3] and illustrate the ability of the tellurium octet to expand to incorporate 12 electrons in the valence shell. Tellurium(VI) compounds have been generated by oxidative addition of fluorine across the tellurium of a 10-Te-4 species. Corresponding selenium and sulfur analogues are known as well.[4]

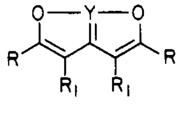


**1**

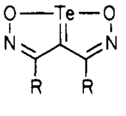


**2**

In principle, 10-Y-3 compounds (Y = S, Se, Te) should be capable of oxidative addition across the central element to give 12-Y-5 compounds. 1,6-Dioxa-6a-thiapentalenes (**3a**)[5] and 1,6-dioxa-6a-selenapentalenes (**3b**),[5b,6] both 10-Y-3 compounds, undergo halogen substitution of the pentalene ring when exposed to halogens,[5a] not oxidative addition. The corresponding tellurium compounds **3c** are unknown, although 2,5-diaza-1,6-dioxa-6a-tellurapentalenes (**4**) have been described.[7]



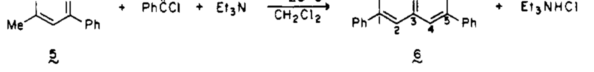
**3a**, Y = S
**b**, Y = Se
**c**, Y = Te



**4**

We wish to report the synthesis and structure of the first 12-Te-5 compounds, pertelluranes **7–10**, from the addition of bromine and chlorine across the tellurium atom of 2,5-diphenyl-1,6-dioxa-6a-tellurapentalene (**6**). The pertelluranes are stable compounds with interesting structural and chemical features.

The dioxatellurapentalene **6** is readily prepared by the reaction shown in eq 1 in 39% yield as a yellow solid, mp 169.5–170.5 °C.[8,9] Compound **6** has been characterized



**5** **6** (1)

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[1] (a) Fötsch, W.; Sladky, F. *J. Chem. Soc., Chem. Commun.* **1980**, 927. (b) Lenty, D.; Pritzkow, J.; Seppett, K, *Inorg. Chem.* **1978**, *17*, 1926.

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[4] Michalak, R. S.; Martin, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 1683.

[5] (a) Reid, D. H.; Webster, R. G. *J. Chem. Soc., Chem. Commun.* **1972**, 1283. (b) Reid, D. H.; Webster, R. G. *J. Chem. Soc. Perkin Trans. 1* **1975**, 775.

[6] (a) Gleiter, R.; Gygax, R. In "Topics in Current Chemistry"; Springer-Verlag: Berlin, 1976; Vol. 63. (b) Gerson, F.; Gleiter, R.; Ohya-Nishiguchi, H. *Helv. Chim. Acta* **1977**, *60*, 1220.

[7] Perrier, M.; Vialle, J. *Bull. Soc. Chim. Fr.* **1971**, 4591.

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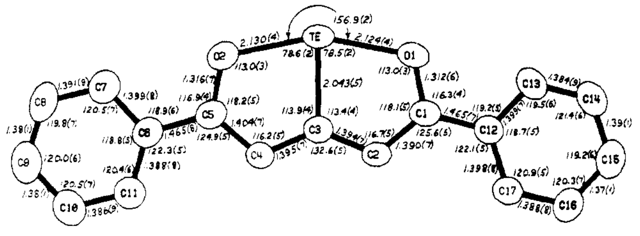
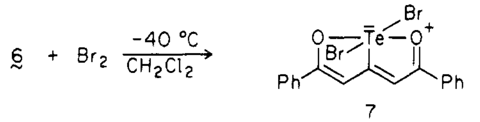


**Figure 1.** Bond lengths and angles with estimated standard deviations in parentheses.

by a single-crystal X-ray diffraction study, the results of which are shown in Figure 1.[10] The bicyclic ring is planar with the C–C bonds within 1$\sigma$ of the aromatic value of 1.394 Å and with the C–O bonds intermediate between single-bond (1.36 Å) and double-bond (1.22 Å) values.[11] The Te–C bond is somewhat shorter (2.043 Å) than that observed for 5 (2.081 Å).[8]

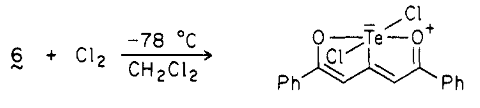
Compound 6 is quite stable to acidic and basic hydrolyses, surviving both hot 3 N HCl and 1 N KOH. The material appears to undergo slow air oxidation on either silica or alumina plates. Electrochemically, 6 shows $E_{p_a}$ at +1.36 V (vs. SCE) at a platinum disk electrode in $CH_2Cl_2$ with 0.1 M $Bu_4NBF_4$ as a supporting electrolyte and $E_{p_c}$ at −1.50 V.

When 1 equiv of bromine was added to 6 as shown in eq 2, a deep magenta solution was obtained from which



(2)

7



(3)

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small crystals of 12-Te-5 pertellurane 7 were isolated in 99% yield, mp 229–230 °C.[12] The specific conductances of solutions of 7 from 1.0 × 10$^{-5}$ to 3.0 × 10$^{-3}$ M (saturated solution) in $CH_2Cl_2$ were all less than 0.5 $\mu\Omega^{-1}$ cm$^{-1}$, indicative of a nonconductive, presumably covalent structure. In contrast, a 1.0 × 10$^{-4}$ M solution of $n$-$Bu_4NBr$ showed a specific conductance of 37 $\mu\Omega^{-1}$ cm$^{-1}$.

Similar behavior was observed for the addition of a $CCl_4$ solution of chlorine to 6 at −78 °C, as shown in eq 3, from which 8 was isolated as small, green crystals, mp 178–180.5 °C.[13]

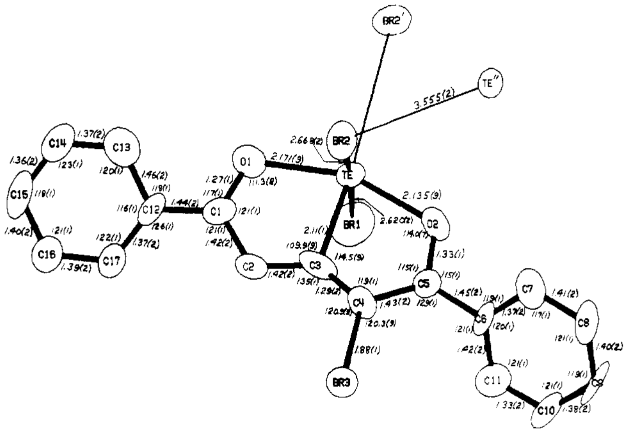
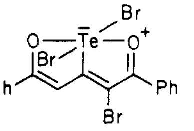
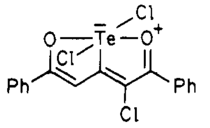


**Figure 2.** Bond lengths and angles with estimated standard deviations in parentheses. Atom Br2′ is related by symmetry $x$, $^1/_2 - y$, $-^1/_2 + z$. Atom Te″ is related by symmetry $x$, $^1/_2 - y$, $^1/_2 + z$.

At 0 °C or warmer, a second equivalent of bromine or chlorine reacted with 7 and 8, respectively, to give the products of ring halogenation, 9[14] and 10.[15] Suitable



9



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crystals of 9 (mp 198–198.5 °C were grown for a single-crystal X-ray crystallographic study, the results of which are shown in Figure 2.[16]

The coordination about Te in 9 is distorted octahedral with the position trans to the Te–C bond occupied by a long, intermolecular Te···Br2′ bond (represented by the thin bonds in Figure 2). The distance (3.355 Å) is considerably less than the sum of van der Waals radii (3.91 Å).[17] The umbrella shape of the five strong ligands to Te can be attributed to the steric influence of a lone pair of electrons on Te. The bicyclic ring in 9 is planar. The Te–C bond is significantly longer in 9 (2.11 Å) than in 6.

Chemically, the pertellurane dibromides 7 and 9 function as mild oxidants for ethylmercaptan, benzenethiol, and benzeneselenol, giving quantitative yields of diethyl di-

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(8) For the preparation of 5: Detty, M. R.; Murray, B. J.; Smith, D. L.; Zumbulyadis, N. *J. Am. Chem. Soc.* **1983**, *105*, 875.

(9) $^1$H NMR ($CDCl_3$) $\delta$ 8.15 (s, 2 H), 8.05 (m, 4 H), 7.47 (m, 6 H); IR (KBr) 1515 (s) cm$^{-1}$; UV ($CH_2Cl_2$) $\lambda_{max}$ 424 nm (log $\epsilon$ 4.61); $^{13}$C NMR ($CDCl_3$) $\delta$ 181.0 ($C_1$, $C_5$), 180.5 ($C_3$), 107.7 ($C_2$, $C_4$); field-desorption mass spectrum (FDMS), $m/e$ 378 ($C_{17}H_{12}O_2{}^{130}Te$). Anal. Calcd for $C_{17}H_{12}O_2Te$: C, 54.3; H, 3.2; Te, 33.9. Found: C, 54.0, H, 3.3; Te, 33.5.

(10) Crystals of 6 form in the monoclinic space group $P2_1$ with $a$ = 15.620 (3) Å, $b$ = 5.782 (1) Å, $c$ = 7.751 (2) Å, $\beta$ = 91.08 (2) Å, $V$ = 699.9 (4) Å$^3$, and $Z$ = 2. The intensities of 2220 independent reflections were measured ($2\theta < 60°$) and all were included in the refinement of the structure. The location of the tellurium atoms was obtained from a Patterson map. A Fourier electron-density map calculated with phases from the Te atom positions yielded seven additional atoms. The remaining 12 non-hydrogen atoms and all the hydrogen atoms were obtained from subsequent difference electron-density maps. Least-squares refinement of the complete structure converged with $R$ = 0.0545 and $R_w$ = 0.0416.

(11) Sutton, L. E. "Tables of Interatomic Distances and Configurations in Molecules and Ions, Supplement", Chemical Society: London, 1965.

(12) IR (KBr) 1595, 1540 (s) cm$^{-1}$; UV ($CH_2Cl_2$) $\lambda_{max}$ 330 (log $\epsilon$ 4.146), 547 nm (4.505); FDMS, $m/e$ 536 ($C_{17}H_{12}Br_2O_2{}^{130}Te$), 457 ($M^+$ − Br), 378 ($M^+$ − 2 Br). Anal. Calcd for $C_{17}H_{12}Br_2O_2Te$: C, 38.1; H, 2.3; Te, 23.8; Br, 29.8. Found: C, 37.8; H, 2.2; Te, 22.3; Br, 29.6.

(13) IR (KBr) 1590, 1550 (s) cm$^{-1}$; UV ($CH_2Cl_2$) $\lambda_{max}$ 315 (log $\epsilon$ 4.28), 544 nm (4.50); FDMS, $m/e$ 448 ($C_{17}H_{12}Cl_2O_2{}^{130}Te$), 413 ($M^+$ − Cl), 378 ($M^+$ − 2 Cl). Anal. Calcd for $C_{17}H_{12}Cl_2O_2Te$: C, 45.7; H, 2.7; Te, 28.6. Found: C, 45.9; H, 2.6; Te, 28.9.

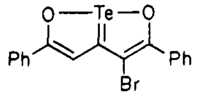
(14) $^1$H NMR ($CDCl_3$) $\delta$ 8.13 (m, 4 H), 7.83 (s, 1 H), 7.60 (m, 6 H); IR (KBr) 1600, 1550 (s) cm$^{-1}$; UV ($CH_2Cl_2$) $\lambda_{max}$ 340 (log $\epsilon$ 4.28), 555 nm (4.57); FDMS, $m/e$ 614 ($C_{17}H_{11}Br_3O_2{}^{130}Te$), 535 ($M^+$ − Br), 456 ($M^+$ − 2 Br). Anal. Calcd for $C_{17}H_{11}Br_3O_2Te$: C, 33.2; H, 1.8. Found C, 33.4; H, 1.9.

(15) mp 188–192 °C dec; $^1$H NMR ($CDCl_3$) $\delta$ 8.30 (m, 4 H), 7.92 (s, 1 H), 7.65 (m, 6 H); IR (KBr) 1590, 1550 (s) cm$^{-1}$; UV ($CH_2Cl_2$) $\lambda_{max}$ 315 (log $\epsilon$ 4.25), 548 nm (4.58); FDMS, $m/e$ 482 ($C_{17}H_{11}Cl_3O_2{}^{130}Te$), 412 ($M^+$ − Cl) (small $m/e$ 516 ($C_{17}H_{10}Cl_4O_2{}^{130}Te$)).

(16) Crystals of 9 form in the monoclinic space group $P2_1/c$ with $a$ = 20.922 (2) Å, $b$ = 11.413 (6) Å, $c$ = 7.557 (2) Å, $\beta$ = 96.61 (1) Å, $V$ = 1793 (2) Å$^3$, and $Z$ = 4. The intensities of 3156 independent reflections ($2\theta$ < 50°) were measured; of these 1972 had $I > \sigma(I)$ and were included in the refinement of the structure. The tellurium atom position was obtained from a Patterson map and the other atoms from subsequent difference electron-density maps. Hydrogen atoms were included at calculated positions but were not refined. Refinement was complicated by a disorder involving molecules with a bromine bonded to C2 rather than C4. This merely requires flipping the molecule over and occurs with about 5% of the molecules. The different spatial requirements for this disorder cause a small shift in the positions of the other atoms. Consequently, the atomic positions and bond distances in this structure are not well determined, and the final agreement indices, $R$ = 0.080 and $R_w$ = 0.095, are higher than usual.

(17) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

sulfide, diphenyl disulfide, and diphenyl diselenide, respectively, as well as reduction products 6 and 11. Diphenyl telluride is oxidized to diphenyl telluroxide with 7, but diphenyl selenide is unreactive toward 7. The pertellurane dibromides and dichlorides do not react with olefins in $CH_2Cl_2$ after 48 h in the dark at ambient temperature, although irradiation leads to small amounts of allylic halides. Compounds 9 and 10 are reduced with hydrazine to give 11[18] and 12[19] in 71% and 89% yields,



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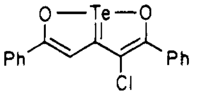

12

respectively. All of the pertelluranes were susceptible to decomposition by hydrolysis.

Attempts to induce oxidative additions of iodine to 6 failed, as did attempts to iodinate the pentalene ring of 7 and 8. This is somewhat surprising in view of the traditional stability of $RTeI_3$ and $R_2TeI_2$ compounds.[20]

**Acknowledgment.** We thank Dr. Thomas H. Whitesides and Dr. William N. Washburn for many helpful discussions.

**Registry No.** **5**, 87761-66-8; **6**, 87761-67-9; **7**, 87761-68-0; **8**, 87761-69-1; **9**, 87761-70-4; **10**, 87761-71-5; **11**, 87761-72-6; **12**, 87761-73-7; PhCOCl, 98-88-4; ethylmercaptan, 75-08-1; benzenethiol, 108-98-5; benzeneselenol, 645-96-5; diethyl disulfide, 110-81-6; diphenyl disulfide, 882-33-7; diphenyl diselenide, 1666-13-3; diphenyl telluride, 1202-36-4; diphenyl telluroxide, 51786-98-2; hydrazine, 302-01-2.

**Supplementary Material Available:** Tables of positional and thermal parameters (Tables I and II for 6, Tables III and IV for 9) and a table of bond angles about Te for 9 (Table V) (5 pages). Ordering information is given on any current masthead page.

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[18] mp 166–167.5 °C; $^1H$ NMR ($CDCl_3$) δ 8.20 (s, 1 H), 8.10 (m, 2 H), 7.90 (m, 2 H), 7.50 (m, 6 H); IR (KBr) 1500 $cm^{-1}$; UV ($CH_2Cl_2$) $\lambda_{max}$ 426 nm (log ε 4.28); FDMS, *m/e* 456 ($C_{17}H_{11}BrO_2{}^{130}Te$). Anal. Calcd for $C_{17}H_{11}BrO_2Te$: C, 44.9; H, 2.4; Te, 28.1. Found: C, 44.7; H, 2.4; Te, 27.3.

[19] mp 150–152.5 °C; $^1H$ NMR ($CDCl_3$) δ 8.20 (s, 1 H), 8.02 (m, 4 H), 7.50 (m, 6 H); IR (KBr) 1525 $cm^{-1}$; UV ($CH_2Cl_2$) $\lambda_{max}$ 427 nm (log ε 4.505); FDMS, *m/e* 412 ($C_{17}H_{11}ClO_2{}^{130}Te$). Anal. Calcd for $C_{17}H_{11}ClO_2Te$: C, 49.8; H, 2.7. Found: C, 49.7; H, 2.8.

[20] Irgolic, K. J. "The Organic Chemistry of Tellurium"; Gordon and Breach: New York, 1974.

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# Chemical Modification of Deoxyribonucleic Acids: A Direct Study by Carbon-13 Nuclear Magnetic Resonance Spectroscopy

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The chemical modifications of salmon sperm and salmon testes DNAs with 90% $^{13}C$-enriched methyl methanesulfonate have been directly studied by $^{13}C$ NMR and $^{31}P$ NMR. This direct stable isotope approach eliminates all tedious degradation and separation processes for determining the reactive sites and product distribution in studying the in vitro interaction between biological macromolecules and bioactive compounds. Seven methylated products, 7-methyldeoxyguanosine, 1-methyldeoxyadenosine, 3-methyldeoxycytidine, 1-methyldeoxyguanosine, 3-methylthymidine, methyl phosphodiester, and methyl phosphotriester were determined by comparison with model compounds and extensive study of the chemical properties of the methylated DNA. The relative specificity of the methylation reactions may correlate with the DNA conformation.

Chemical modification of polynucleotides and nucleic acids[1,2] is one of the promising approaches for studying the structure and function of nucleic acids.[3-14] It is evident that the success of this approach relies upon the accurate determination of the reaction specificity, sites of modification, and product distribution. Although the radioisotope-labeling method has generally been used because of its ultrahigh sensitivity, this approach, at best, can merely detect the degree of overall modification. In order to obtain structural information on a covalent interaction, it is necessary to carry out a series of enzymatic and acid-catalyzed hydrolyses followed by chromatography or electrophoresis under acidic or alkaline conditions to separate all modified bases and nucleosides, using radioactivity, fluorescence, or ultraviolet detector.[15,16] This

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