Details of the individual data collections are given in Table V. Selected results are presented in Tables I–IV, while full crystallographic data appear in Tables S1–S10 in the supplementary material.

**X-ray Structure Determination of Compounds 3 and 5.** Suitable crystals for X-ray structural analysis of compound 3 (black, rectangular, 0.40 × 0.25 × 0.20 mm) and 5 (black, rectangular, 0.35 × 0.20 × 0.20 mm) were glued to the tips of glass fibers. The crystals were mounted and optically centered on a modified Picker four-circle diffractometer equipped with a gas-stream low-temperature device and graphite-monochromatized Mo source.[45] Accurate unit cell parameters and orientation matrices were obtained by a least-squares fit to the automatically centered settings of 38 reflections for 3 and 28 reflections for 5, respectively, and are listed in Table V together with other experimental details. A $\theta/2\theta$ scan mode was employed to collect one hemisphere $(h,\pm k,\pm l)$ of data with the maximum $2\theta$ of 50° for 3 and one quadrant $(h,k,\pm l)$ of data with the maximum $2\theta$ of 45° for 5, at low temperature (128 K). Three standard reflections were monitored for every 97 reflections collected and showed no significant variations throughout the data collection. Intensities were derived from an analysis of scan profiles. The data were corrected for Lorentz and polarization effects. A $\psi$-scan procedure was used for an empirical absorption correction.

The structures were solved in the monoclinic space groups $C2/c$ for 3 and $P2_1/n$ (No. 14) for 5 by heavy-atom methods of SHELX86, which revealed the positions of chromium and most of the carbon atoms. The remaining non-hydrogen atoms were located from subsequent difference electron density maps. This was followed by several cycles of full-matrix least-squares refinement. Hydrogen atoms were included as fixed contributors to the final refinement cycles. The positions of hydrogen atoms were calculated on the basis of idealized geometry and bond length (C–H = 1.00 Å). For methyl groups, at least one of the hydrogen atom positions was located from the difference-Fourier map.

For compound 3, in the final cycles of least-squares refinement, all non-hydrogen atoms were refined with anisotropic thermal coefficients. The refinement converged at $R = 0.031$ and $R_w = 0.053$. For compound 5, an unidentified disordered solvent molecule was located at the inversion center. Attempts to model the solvent molecule were not successful. Crystal-packing diagrams show the solvent molecules occupying channels down the inversion center. Three strong peaks with reasonable C–C distances were arbitrarily assigned as carbon atoms with half-occupancies and were included as fixed contributors in the final cycles of refinement. The final $R$ factors are 0.066 and 0.101.

**Acknowledgment.** We thank the UCLA Academic Senate, Committee on Research, for support of this research.

**Supplementary Material Available:** Tables of positional parameters, bond distances, bond angles, and thermal parameters for compounds 3 and 5 (10 pages); listings of observed and calculated structure factors for compounds 3 and 5 (17 pages). Ordering information is given on any current masthead page.

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# Preparation of Symmetrical Di-1-alkynyl Tellurides and Diynes by Reduction of $TeCl_4$ with 1-Alkynyllithium Reagents

Robert W. Gedridge, Jr.,*[†] Lambert Brandsma,*[‡] Robin A. Nissan,[†] Hermann D. Verkruijsse,[‡]
Sjoerd Harder,[‡] Robertus L. P. de Jong,[‡] and Charles J. O'Connor[†,§]

*Chemistry Division, Research Department, Naval Weapons Center, China Lake, California 93555,*
*and Department of Synthetic Organic Chemistry, Debye Research Institute, University of Utrecht,*
*Padualaan 8, 3584 CH Utrecht, The Netherlands*

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Di-1-alkynyl tellurides ($(RC\equiv C)_2Te$, where R = Me, Et, *n*-Pr, *t*-Bu, $Me_3Si$, Ph) have been prepared in 42–69% yields by the reaction of $TeCl_4$ with 4 equiv of the corresponding 1-alkynyllithium reagents ($RC\equiv CLi$). Diynes ($RC\equiv CC\equiv CR$, where R = *t*-Bu, $Me_3Si$, Ph) were isolated as major byproducts from these reactions. While tetra-1-alkynyltellurium(IV) or other possible organotellurium(IV) intermediates were not isolated, it is proposed that these intermediates decompose by a reductive-elimination pathway to afford $(RC\equiv C)_2Te$ and $RC\equiv CC\equiv CR$. These organotellurium compounds have been characterized by IR and $^1H$, $^{13}C$, and $^{125}Te$ NMR spectroscopies.

## Introduction

Organotellurium compounds have attracted a great deal of interest as useful reagents in organic chemistry.[1] Even though many diorganyl tellurides ($R_2Te$) have been extensively studied, little attention has been given to alkynyl tellurides until recently.[2] Di-1-alkynyl sulfides are readily obtainable from ether suspensions or solutions of 1-alkynyllithium reagents and sulfur dichloride (eq 1).[3] Di-1-

$$2RC\equiv CLi + SCl_2 \xrightarrow[-80\ ^\circ C]{Et_2O/hexane} (RC\equiv C)_2S + 2LiCl \qquad (1)$$

propynyl selenide, $(MeC\equiv C)_2Se$, was obtained in a good yield by reacting 1-propynyllithium with a cold solution

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[†] Naval Weapons Center.

[‡] University of Utrecht.

[§] Current address: Chemistry Department, University of New Orleans, New Orleans, LA 70148.

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of $SeCl_4$ in tetrahydrofuran (THF) at temperatures in the range of −20 to +20 °C.[4] A small amount of the 2,4-hexadiyne, $MeC{\equiv}CC{\equiv}CMe$, was isolated from this reaction. Tetra-1-propynylselenium(IV), $(MeC{\equiv}C)_4Se$, is a possible intermediate in this reaction (eq 2). Recently,

$$4MeC{\equiv}CLi + SeCl_4 \xrightarrow{\text{THF/hexane}} [(MeC{\equiv}C)_4Se] \rightarrow (MeC{\equiv}C)_2Se + MeC{\equiv}CC{\equiv}CMe \quad (2)$$

we reported the isolation and characterization of tetramethyltellurium(IV), $Me_4Te$, from an ether solution of methyllithium and $TeCl_4$.[5] Since other tetraorganotellurium(IV) compounds such as $(CH_2{=}CH)_4Te$[6] and $(Ph)_4Te$[7] are known, we attempted to prepare tetra-1-alkynyltellurium(IV), $(RC{\equiv}C)_4Te$, compounds. However, we were only able to isolate symmetrical di-1-alkynyl tellurides, $(RC{\equiv}C)_2Te$.

Symmetrical dialkyl tellurides ($R_2Te$) are typically prepared in high yields from reaction of $M_2Te$ (M = Li, Na) with 2 equiv of an alkyl halide.[6,8] Diorganyl tellurides have also been obtained by reducing $TeCl_4$ or diorganyltellurium dihalides ($R_2TeX_2$) with Grignard or organyllithium reagents.[1a,6,9] Although many 1-alkynyl alkyl tellurides ($RC{\equiv}CTeR'$) have been prepared,[2a,b,3b,10] symmetrical di-1-alkynyl tellurides have only recently been isolated.[2b,e] We now report the synthesis and spectroscopic characterization of a variety of symmetrical di-1-alkynyl tellurides.

## Results and Discussion

**Synthesis of $(RC{\equiv}C)_2Te$ Compounds.** The reaction of at least 4 equiv of the 1-alkynyllithium reagents with $TeCl_4$ in tetrahydrofuran (THF) or THF/hexane mixtures under an Ar atmosphere produces good yields of $(RC{\equiv}C)_2Te$ (eq 3). In addition, diynes ($RC{\equiv}CC{\equiv}CR$, where

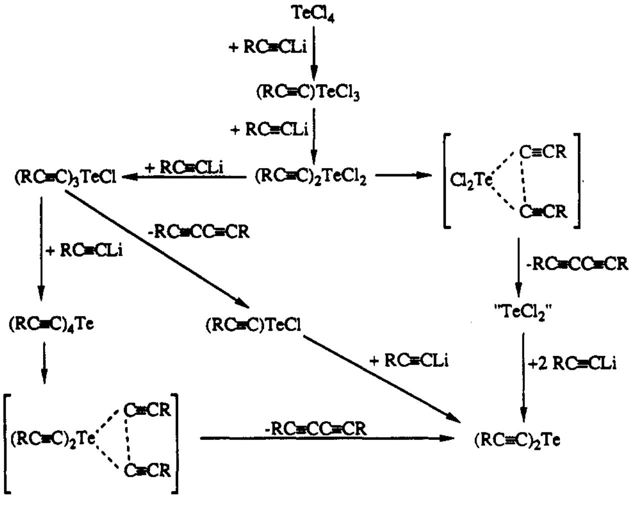
$$4RC{\equiv}CLi + TeCl_4 \xrightarrow{\text{THF/hexane}} (RC{\equiv}C)_2Te + RC{\equiv}CC{\equiv}CR \quad (3)$$

$$R = Me,\ Et,\ n\text{-}Pr,\ t\text{-}Bu,\ Ph,\ Me_3Si$$

R = t-Bu, $Me_3Si$, Ph) were isolated as major byproducts. Recently, a variety of $(RC{\equiv}C)_2Te$ compounds has been prepared by a reductive dialkynylation of $TeCl_4$ with lithium amides and terminal acetylenes via tellurium diamide, $(R_2N)_2Te$, intermediates.[2e] Furthermore, $(PhC{\equiv}C)_2Te$ can also be prepared in good yields by reacting $PhC{\equiv}CLi$ with Te metal followed by $PhC{\equiv}CBr$.[2b]

In our first attempt, finely powdered $TeCl_4$ was added to a suspension of 4 equiv of $EtC{\equiv}CLi$ in diethyl ether.

Scheme I



After 2 h of reflux, the products were isolated from the ether layer after aqueous workup. The small residue which remained after removal of the solvent under vacuum underwent extensive decomposition upon attempted distillation, and only a small amount of $(EtC{\equiv}C)_2Te$ was isolated.

In another experiment, a solution of $TeCl_4$ in THF at −55 °C was added to a solution of excess (20–30% molar) $(t\text{-}Bu)C{\equiv}CLi$ in THF and hexane at −20 °C. The mixture was then warmed to 5 °C and the solvent was removed under vacuum using a temperature bath not exceeding 15 °C. The crude products were extracted with pentane, and the pentane was removed under vacuum. In this experiment, the yield of the remaining extracted organic products was much smaller than the theoretically expected amount. However, when the reaction mixture was heated to 60 °C for 1 h and after the crude products were flash-distilled under high vacuum, 85% of the theoretical amount of extractable material was isolated. A similar result was obtained after the reaction mixture was heated at 40 °C for 30 min and the products were isolated from the organic layer in an aqueous workup. $^1H$ and $^{13}C$ NMR spectra of the crude products from these experiments revealed the presence of only $(t\text{-}Bu)C{\equiv}CC{\equiv}C(t\text{-}Bu)$ and $((t\text{-}Bu)C{\equiv}C)_2Te$ in approximately a 1:1 ratio.

In an attempt to isolate $(PhC{\equiv}C)_4Te$ by a low-temperature route, $TeCl_4$ was reacted with 4 equiv of $PhC{\equiv}CLi$ in THF at −78 °C. The reaction mixture was warmed to 0 °C, and all the solvent was removed under vacuum. The orange residue was extracted with pentane at 0 °C. After removal of the solvent under vacuum, $^{13}C$ and $^{125}Te$ NMR characterization of the crude product revealed only the presence of $(PhC{\equiv}C)_2Te$ and $PhC{\equiv}CC{\equiv}CPh$. These products were also observed from the reaction of $TeCl_4$ with 4 equiv of $PhC{\equiv}CMgBr$.[11] No evidence for $(PhC{\equiv}C)_4Te$ or any other organotellurium(IV) compound was observed. These observations suggest that the reaction mixtures should be heated to ensure complete reaction and that if $(RC{\equiv}C)_4Te$ compounds are formed, they are unstable even at low temperatures.

**Mechanism.** Since high yields of an equimolar mixture of $(t\text{-}Bu)C{\equiv}CC{\equiv}C(t\text{-}Bu)$ and $((t\text{-}Bu)C{\equiv}C)_2Te$ were obtained and $(t\text{-}Bu)C{\equiv}CCl$ does not react with $(t\text{-}Bu)C{\equiv}CLi$ in the absence of a Cu catalyst to form $(t\text{-}Bu)C{\equiv}CC{\equiv}C(t\text{-}Bu)$, reductive-elimination pathways of organotellurium(IV) chloride intermediates to form $(t\text{-}Bu)C{\equiv}CCl$

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Table I. NMR Chemical Shifts and Coupling Constants[a]

| compd | NMR spectra | | |
|---|---|---|---|
| | $^1H$ | $^{13}C$ | $^{125}Te^b$ |
| $(CH_3C\equiv C)_2Te$ | 1.67 (s, $CH_3$) | 5.40 (q, $CH_3$, $^3J_{TeC}$ = 186.7, $^1J_{CH}$ = 131.7)<br>31.4 (q of q, $\equiv CTe$, $^1J_{TeC}$ = 538.5, $^3J_{CH}$ = 6.2, $^5J_{CH}$ = 2)<br>109.3 (q, $CH_3C\equiv$, $^2J_{TeC}$ = 112.4, $^2J_{CH}$ = 10.1) | 338 (m of 5, $^4J_{TeH}$ = 5) |
| $(CH_3CH_2C\equiv C)_2Te$ | 2.13 (q, $CH_2C\equiv$, $^3J_{HH}$ = 7.5)<br>0.83 (t, $CH_3$) | 13.9 (q of t, $CH_3$, $^1J_{CH}$ = 128.6, $^2J_{CH}$ = 5.3)<br>14.8 (t of q, $CH_2CH_2$, $^1J_{CH}$ = 131.0, $^2J_{CH}$ = 4.5)<br>31.9 (t of t, $\equiv CTe$, $^1J_{TeC}$ = 537.7, $^3J_{CH}$ = 5.8, $^5J_{CH}$ = 2)<br>115.1 (q of t, $CH_2C\equiv$, $^2J_{TeC}$ = 112.0, $^2J_{CH}$ = 9.9, $^3J_{CH}$ = 6) | 332 (m of 5, $^4J_{TeH}$ = 5) |
| $(CH_3CH_2CH_2C\equiv C)_2Te$ | 2.15 (t, $CH_2C\equiv$, $^3J_{HH}$ = 7.0)<br>1.26 (m of 6, $CH_2$)<br>0.76 (t, $CH_3$, $^3J_{HH}$ = 7.4) | 13.4 (q of t of t, $CH_3$, $^1J_{CH}$ = 125.4)<br>22.4 (t of q of t, $CH_2CH_2$, $^1J_{CH}$ = 128.7, $^2J_{CH}$ = 4, $^2J_{CH}$ = 4)<br>23.0 (t of q of t, $CH_2C\equiv$, $^1J_{CH}$ = 130.4, $^3J_{CH}$ = 6.1, $^2J_{CH}$ = 4.1)<br>32.5 (t of t, $\equiv CTe$, $^1J_{TeC}$ = 538.1, $^3J_{CH}$ = 5.8, $^5J_{CH}$ = 2)<br>113.8 (t of t, $CH_2C\equiv$, $^2J_{TeC}$ = 111.6, $^2J_{CH}$ = 10.0, $^3J_{CH}$ = 6.0) | 332 (m of 5, $^4J_{TeH}$ = 5) |
| $((CH_3)_3CC\equiv C)_2Te$ | 1.06 (s, $CH_3$) | 29.5 (m of 8, $(CH_3)_3C$, $^2J_{CH}$ = 131.7)<br>30.9 (q of septets, $CH_3$, $^1J_{CH}$ = 127.5, $^3J_{CH}$ = 4.6)<br>31.5 (s, $\equiv CTe$, $^1J_{TeC}$ = 538.1)<br>121.4 (m of 8, $(CH_3)_3CC\equiv$, $^2J_{TeC}$ = 111.6, $^3J_{CH}$ = 5.2) | 321 (s) |
| $((CH_3)_3SiC\equiv C)_2Te$ | 0.02 (s, $CH_3$) | −0.19 (q, $CH_3$, $^1J_{CH}$ = 120.2)<br>60.9 (s, $\equiv CTe$, $^1J_{TeC}$ = 538.5)<br>123.2 (s, $SiC\equiv$, $^2J_{TeC}$ = 115.6) | 385 (s) |
| $((C_6H_5)C\equiv C)_2Te$ | 6.8 (m, 3 H)<br>7.3 (m, 2 H) | 44.8 ($\equiv CTe$, $^1J_{TeC}$ = 555.7)<br>112.9 (s, $C\equiv CTe$, $^2J_{TeC}$ = 110.4)<br>123.4<br>128.4<br>129.0<br>132.3 | 361 (s) |
| $CH_3TeC\equiv CTeCH_3$[c] | 1.61 (s, $CH_3$) | −13.84 (q, $CH_3$, $^1J_{CH}$ = 143.6, $^1J_{TeC}$ = 155.9)<br>66.41 (q, $C\equiv C$, $^3J_{CH}$ = 4.5, $^1J_{TeC}$ = 556.0, $^2J_{TeC}$ = 116.2) | 215 (q, $^2J_{TeH}$ = 25.8) |

[a] Chemical shifts in ppm and coupling constants in Hz. Abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). [b] All $^{125}Te$ chemical shifts were referenced to neat $Me_2Te$ and recorded at room temperature with 1 M telluride in $C_6D_6$. [c] Reference 2c.

are improbable. It is proposed that either $(RC\equiv C)_4Te$ or some organotellurium(IV) chloride intermediate decomposes by a reductive-elimination pathway by forming a new carbon–carbon bond to produce diynes and $(RC\equiv C)_2Te$ compounds (Scheme I). Similarly, studies by Barton and co-workers indicated tetraaryltellurium(IV) compounds exchange ligands by a fast nonradical process prior to thermal decomposition by a reductive coupling pathway to afford diaryl tellurides and biaryls as the major products.[12] The formation of a new carbon–carbon bond between reductively eliminated ligands is a type of organometallic reaction that has an important role in many metal-based catalytic cycles.

**NMR Spectra.** The NMR data for the $(RC\equiv C)_2Te$ compounds are reported in Table I. Although $^1H$ NMR data have been reported for various symmetrical and unsymmetrical 1-alkynyl tellurides,[2a,b,10] very little information on the $^{13}C$ and $^{125}Te$ NMR spectra for these compounds is known. The $^{13}C$ NMR spectra of $CH_2{=}CHC\equiv CTeR$ (R = Me, Et) reveal that $C_\alpha$ bound to Te has a chemical shift between 46 and 49 ppm while $C_\beta$ resonates between 109 and 111 ppm.[13] The assignments for the sp carbons were based on the observation of a doublet for $C_\beta$ due to spin–spin coupling ($^2J_{CH}$ = 9 Hz) with the methine proton.

The $^{13}C\{^1H\}$ spectra for the $(RC\equiv C)_2Te$ compounds exhibit distinct $^{125}Te$ satellites for the sp carbons between 109 and 123 ppm. Initially, we incorrectly assigned these peaks to the $C_\alpha$ bound to Te. The 111–116-Hz $J_{TeC}$ coupling constants measured for these peaks were smaller than the measured 156-Hz $^1J_{TeC}$ coupling constant for the $sp^3$ carbons in $MeTeC\equiv CTeMe$.[2c] Further investigation revealed that the peaks in the 31–61 ppm range for the $(RC\equiv C)_2Te$ compounds exhibited $^{125}Te$ satellites with significantly larger $J_{TeC}$ coupling constants (538–556 Hz), as expected for sp carbons with a high s character. Therefore, we assign the peaks in the 31–61 ppm range to the $C_\alpha$ carbons and the peaks in the 109–123 ppm range to the $C_\beta$ carbons.

To our knowledge, the $^1J_{TeC}$ coupling constants (538–556 Hz) measured for the $(RC\equiv C)_2Te$ compounds are the largest reported. While the literature data for $^1J_{TeC}$ coupling constants are limited, values have been reported for a variety of di- and polytelluroethers.[14] The $^1J_{TeC}$ coupling constants for MeTe and $CH_2Te$ in $MeTe(CH_2)_nTeMe$ are between 150 and 180 Hz except for $RTeCH_2TeR$, for which the values are 205–210 Hz.[14] In aromatic substituents, the ipso carbons exhibit $^1J_{TeC}$ coupling constants between 280 and 332 Hz.[14] The larger $^1J_{TeC}$ coupling constants measured for the $(RC\equiv C)_2Te$ compounds coincide with the expected increase in s character of an sp carbon bound to Te. The $^2J_{TeC}$ coupling constants (111–116 Hz) are considerably larger than those measured (30–60 Hz) in di- and polytelluroethers.[14] Reinvestigation of the $^{13}C\{^1H\}$ NMR spectrum of $MeTeC\equiv CTeMe$ (see Table I) revealed $^1J_{TeC}$ (556 Hz) and $^2J_{TeC}$ (116 Hz) coupling constants for the sp carbons analogous to those measured for the $(RC\equiv C)_2Te$ compounds. We did not observe the $^3J_{TeC}$ coupling constants for the $(RC\equiv C)_2Te$ compounds.

The $^1H$-coupled $^{13}C$ NMR spectra for $(RC\equiv C)_2Te$ compounds revealed long-range spin–spin coupling through the metal center. The $C_\beta$ sp carbons in $(CH_3C\equiv C)_2Te$ and $(CH_3CH_2C\equiv C)_2Te$ exhibited a quartet ($^2J_{CH}$ = 10.1 Hz) and a triplet of quartets ($^2J_{CH}$ = 9.9, $^3J_{CH}$ = 6 Hz) (Figure 1A and Figure 2A), respectively. The $C_\alpha$ sp carbons in $(CH_3C\equiv C)_2Te$ and $(CH_3CH_2C\equiv C)_2Te$ exhibited a quartet of quartets ($^3J_{CH}$ = 6.2, $^5J_{CH}$ = 2 Hz) and a triplet of triplets ($^3J_{CH}$ = 5.8, $^5J_{CH}$ = 2 Hz) (Figure 1B and 2B), respectively. These splitting patterns unequivocally in-

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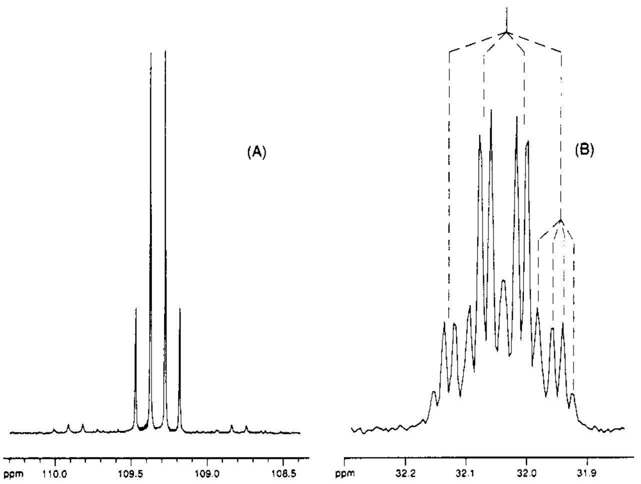

**Figure 1.** $^1$H-coupled $^{13}$C NMR spectrum (100 MHz) of $(CH_3C{\equiv}C)_2Te$ for (A) the $C_\beta$ sp carbon (quartet) and (B) the $C_\alpha$ sp carbon (quartet of quartets).

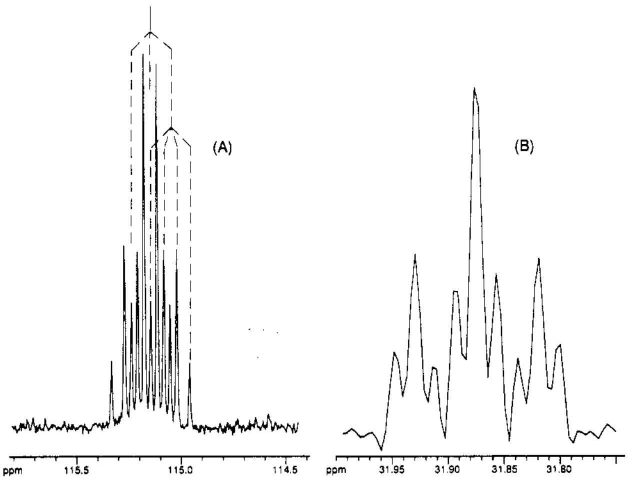

**Figure 2.** $^1$H-coupled $^{13}$C NMR spectrum (100 MHz) of $(CH_3CH_2C{\equiv}C)_2Te$ for (A) the $C_\beta$ sp carbon (triplet of quartets) and (B) the $C_\alpha$ sp carbon (triplet of triplets).

dicated long-range (five-bond) coupling through the Te atom. Spin–spin CH coupling through the metal center was also observed in $MeTeC{\equiv}CTeMe$[2c] and saturated tellurides such as $Et_2Te$.[15]

$^{125}$Te NMR studies of a variety of tellurium compounds[14,16] indicate that substitution $\gamma$ to the Te atom causes very little shift in the $^{125}$Te resonance and more remote structural changes have little or no effect. Consistent with these previous studies, $\gamma$-substitution from $MeC{\equiv}C$ to $EtC{\equiv}C$ or $n$-$PrC{\equiv}C$ results in only a 6 ppm upfield shift, while a $MeC{\equiv}C$ to $t$-$BuC{\equiv}C$ substitution results in a 17 ppm upfield shift in the $^{125}$Te resonance. Substitution from $MeC{\equiv}C$ to $Me_3SiC{\equiv}C$ results in a more dramatic 47 ppm downfield shift in the $^{125}$Te resonance. Overall, the $^{125}$Te resonances in the $(RC{\equiv}C)_2Te$ compounds are similar to the 376 ppm chemical shift of $Et_2Te$.[16a]

**IR Spectra.** FTIR spectra were collected on neat $(RC{\equiv}C)_2Te$ (R = Et, $n$-Pr, $Me_3Si$) films between KBr plates. For $(RC{\equiv}C)_2Te$ (R = Me, $t$-Bu), spectra were collected in KBr by diffuse reflectance. Analogous to the $C{\equiv}C$ stretch at 2140 cm$^{-1}$ for $(PhC{\equiv}C)_2Te$,[2b] the $C{\equiv}C$ stretch in $(RC{\equiv}C)_2Te$ (R = Et, $n$-Pr) was observed around 2160 cm$^{-1}$. The $C{\equiv}C$ stretch was also observed in this region for $(RC{\equiv}C)_2Te$ (R = Me, $t$-Bu) but split into doublets that may be attributed to crystal field splitting of the solid samples. The $C{\equiv}C$ stretch in $(Me_3SiC{\equiv}C)_2Te$ was assigned to the band at 2079 cm$^{-1}$. The Te–C stretch in the $(RC{\equiv}C)_2Te$ compounds (R = Me, Et, $n$-Pr, $t$-Bu) was observed between 510 and 542 cm$^{-1}$. This is analogous to the reported Te–C stretch in $Me_2Te$ at 528 cm$^{-1}$.[17] However, no resolvable bands in this region were observed for $(Me_3SiC{\equiv}C)_2Te$.

## Experimental Section

**General Procedures.** Organotellurium compounds should be handled with caution, since they are generally malodorous and toxic.[18] Organic solvents were distilled under argon from sodium/benzophenone. Synthesis was carried out under purified argon using inert-atmosphere techniques. Air- and moisture-sensitive materials were transferred inside a helium-filled Vacuum Atmospheres glovebox. These tellurides are air- and light-sensitive. Reaction flasks were wrapped in aluminum foil to minimize exposure to light. $TeCl_4$ was purchased from Alfa and Aldrich. $Me_3SiC{\equiv}CH$, $n$-$PrC{\equiv}CH$, and $PhC{\equiv}CH$ were purchased from Aldrich. The preparation of the other acetylenes and subsequent lithiation of the acetylenes using $n$-BuLi was carried out as described in the literature.[3] Elemental analyses were performed by E + R Microanalytical Laboratory, Inc.

NMR spectra were recorded on $C_6D_6$ solutions with a Bruker AMX-400 spectrometer. $^{125}$Te NMR spectra were recorded on 1 M solutions in $C_6D_6$ at 126.2 MHz, with a 60° pulse, a 3-s receiver delay, and neat $Me_2Te$ as reference at 0 ppm. $^{13}$C spectra were obtained at 100.6 MHz with $^1$H-coupled $^{13}$C spectra obtained under gated decoupling conditions. IR spectra were recorded with a Nicolet 60-SX Fourier transform spectrometer. All spectra were obtained at 4-cm$^{-1}$ resolution using Happ–Genzel apodization and a liquid-$N_2$-cooled mercury cadmium telluride detector/Ge-coated KBr beam splitter for the 6500–450-cm$^{-1}$ range.

**Preparation of $(RC{\equiv}C)_2Te$ (R = Me, Et, $t$-Bu, $Me_3Si$) Followed by an Aqueous Workup.** A suspension of the 1-alkynyllithium reagent (0.25 mol) in 160 mL of hexane and 100 mL of THF was prepared in a 1-L round-bottom, three-necked flask, equipped with a gas inlet, a mechanical stirrer, and a thermometer-outlet combination. The suspension was cooled to −25 °C, and a solution of $TeCl_4$ (0.05 mol) in 40 mL of THF at −55 °C (this solution was made immediately before the addition) was quickly added with vigorous stirring. The solid soon disappeared, and light brown solutions were formed after subsequent heating for 40 min at 45–50 °C in the cases of R = Me, Et. Light yellow solutions were formed in the cases of R = $t$-Bu, $Me_3Si$ after heating to 60 °C for 1 h. The reaction mixtures were then cooled to 0 °C and treated with 200 mL of deoxygenated ice water. The water layers were extracted with pentane, and the organic layers were dried with $MgSO_4$. The solvents were then removed by fractional distillation, and the crude product was isolated by flash distillation (0.5–1 Torr) using a short-path-length still. In the case of R = Me, Et, uncharacterized viscous brown residues remained in the distillation pot. $(RC{\equiv}C)_2Te$ compounds (R = Me, $t$-Bu) were purified by recrystallization at −25 °C in pentane. $(RC{\equiv}C)_2Te$ compounds (R = Et, $Me_3Si$) were purified by fractional vacuum distillation. The diynes $RC{\equiv}CC{\equiv}CR$ (R = $t$-Bu, $Me_3Si$) were obtained as the first fractions in 65% yield and were recrystallized from pentane. The diynes were identified by comparison to authentic samples.[3] Although $MeC{\equiv}CC{\equiv}CMe$ was not observed, $EtC{\equiv}CC{\equiv}CEt$ was detected in the first fractions in small amounts.

**Preparation of $(RC{\equiv}C)_2Te$ (R = $n$-Pr, $Me_3Si$, Ph) Followed by a Nonaqueous Workup.** To a solution of $TeCl_4$ (11 mmol) in 25 mL of THF cooled to −78 °C was added dropwise with vigorous stirring the 1-alkynyllithium reagent (46 mmol) in

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25 mL of THF. The solution was warmed to room temperature slowly and then heated at 55–60 °C for 1 h in the dark. When R = *n*-Pr, Ph, dark orange solutions resulted, while a brown solution resulted when R = $Me_3Si$. The reaction mixtures were then cooled to room temperature, and the solvent was removed under vacuum. The residues were extracted with pentane and the extracts then filtered. The pentane was removed under vacuum, and the crude product was purified by vacuum distillation in the case of $(RC{\equiv}C)_2Te$ (R = *n*-Pr, $Me_3Si$). In the case of $(PhC{\equiv}C)_2Te$, the products were extracted with a 5:1 pentane/toluene solution. After removal of the solvents under vacuum, 90% (based on $TeCl_4$) of the crude products were isolated. The byproduct $PhC{\equiv}CC{\equiv}CPh$ was sublimed out of the crude mixture (30% yield) under dynamic vacuum at 100 °C. However, even after multiple sublimations and extractions we were unable to remove all of the $PhC{\equiv}CC{\equiv}CPh$ to obtain an analytically pure sample of $(PhC{\equiv}C)_2Te$. The problem of separating and purifying $(PhC{\equiv}C)_2Te$ from this mixture has been previously reported.[11]

**$(MeC{\equiv}C)_2Te$.** The light yellow product was purified by recrystallization from pentane (mp = 50–52 °C) and can be fractionally distilled at 110 °C at 15 Torr (42% yield based on $TeCl_4$). Anal. Calcd for $C_6H_6Te$: C, 35.03; H, 2.94; Te, 62.03. Found: C, 35.00; H, 2.95; Te, 61.84. FTIR (diffuse reflectance/KBr): 3178 (m), 3166 (m), 3025 (sh), 2952 (ms), 2909 (s), 2839 (ms), 2721 (w), 2380 (w), 2171 (vs), 2164 (vs), 2034 (m), 1432 (s), 1364 (ms), 1263 (w), 1021 (ms), 997 (vs), 689 (m), 510 (w) $cm^{-1}$.

**$(EtC{\equiv}C)_2Te$.** The light yellow liquid was collected by vacuum distillation at 125 °C at 15 Torr (or 45–46 °C at 0.075 Torr) in 56% yield based on $TeCl_4$. Anal. Calcd for $C_8H_{10}Te$: C, 41.10; H, 4.31; Te, 54.58. Found: C, 41.04; H, 4.60; Te, 54.57. FTIR (neat/KBr plates): 2976 (vs), 2937 (s), 2913 (ms), 2878 (ms), 2838 (w), 2160 (ms), 1454 (m), 1429 (m), 1375 (w), 1312 (vs), 1069 (ms), 1029 (w), 886 (w), 779 (w), 526 (m) $cm^{-1}$.

**$(n\text{-}PrC{\equiv}C)_2Te$.** The pale yellow liquid was distilled at 67–68 °C at 0.075 Torr (69% yield based on $TeCl_4$). Anal. Calcd for $C_{10}H_{14}Te$: C, 45.87; H, 5.39; Te, 48.74. Found: C, 47.62; H, 5.55; Te, 47.24. FTIR (neat/KBr plates): 2962 (vs), 2933 (vs), 2901 (ms), 2871 (s), 2832 (w), 2161 (m), 1712 (w), 1462 (ms), 1425 (w), 1380 (w), 1338 (m), 1325 (w), 1274 (w), 1258 (sh), 1224 (w), 1092 (w), 1076 (w), 1057 (w), 1000 (w), 964 (m), 877 (w), 843 (w), 775 (w), 737 (w), 542 (w) $cm^{-1}$.

**$(t\text{-}BuC{\equiv}C)_2Te$.** The light yellow-green product was purified by recrystallization from pentane (mp = 62–64 °C) and can be fractionally distilled at 130 °C at 15 Torr (62% yield based on $TeCl_4$). Anal. Calcd for $C_{12}H_{18}Te$: C, 49.72; H, 6.26; Te, 44.02. Found: C, 49.88; H, 6.21; Te, 43.91. FTIR (diffuse reflectance/KBr): 3992 (w), 3892 (w), 3333 (w), 3249 (w), 3196 (w), 3080 (sh), 3035 (sh), 2969 (vs), 2928 (vs), 2906 (s), 2866 (s), 2814 (sh), 2802 (sh), 2389 (w), 2288 (w), 2167 (m), 2133 (ms), 1472 (ms), 1453 (s), 1390 (m), 1362 (s), 1248 (s), 1204 (ms), 1030 (m), 930 (m), 911 (m), 744 (ms), 530 (m), 482 (m), 469 (m) $cm^{-1}$.

**$(Me_3SiC{\equiv}C)_2Te$.** The light yellow liquid was collected by vacuum distillation at 135 °C at 15 Torr (60% yield based on $TeCl_4$). Anal. Calcd for $C_{10}H_{18}Si_2Te$: C, 37.30; H, 5.63; Si, 17.44; Te, 39.62. Found: C, 37.46; H, 5.65; Si, 17.42; Te, 39.39. FTIR (neat/KBr plates): 2960 (m), 2899 (w), 2859 (w), 2079 (m), 1409 (w), 1385 (w), 1250 (s), 1090 (w), 844 (vs), 760 (ms), 712 (s), 647 (w) $cm^{-1}$.

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# Synthesis, Characterization, and Acid-Induced Decomposition of the α- and β-Diastereomers of (2-Hydroxyethyl)- and (2-Alkoxyethyl)cobalamins and Cobinamides

Kenneth L. Brown,* Laurent Salmon, and John A. Kirby

*Department of Chemistry, Box CH, Mississippi State University, Mississippi State, Mississippi 39762*

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A series of (alkoxyethyl)cobalt corrinoids ($ROCH_2CH_2CoC$, R = H, $C_6H_5$, $(CH_3)_2CH$, $CH_3$, $CH_3CH_2$, $CF_3CH_2$) has been prepared including the α- and β-diastereomers of the (alkoxyethyl)cobalamins ($ROCH_2CH_2Cbl$'s) and the α- and β-diastereomers of the (alkoxyethyl)cobinamides ($ROCH_2CH_2Cbi$'s). In addition, the deuterated analogue of (β-hydroxyethyl)cobalamin ([1,2-$^2H_4$]-β-$HOCH_2CH_2Cbl$) and the $^{13}C$-enriched analogues of all four of the hydroxyethyl complexes (α- and β-[1,2-$^{13}C_2$]-$HOCH_2CH_2Cbl$'s and α- and β-[1,2-$^{13}C_2$]-$HOCH_2CH_2Cbi$'s) have been prepared. These compounds have been characterized by UV–visible spectroscopy, GC/MS identification of the organic products of their solid-state anaerobic pyrolysis, FAB MS, and $^1H$, $^2H$, $^{13}C$, $^{19}F$, and $^{13}C$-edited $^1H$ NMR spectroscopy. All of the compounds are acid labile, decomposing with strictly first-order kinetics (at a given pH) at pH's of 0–4.4 in aqueous media and in aqueous sulfuric acid. The products of this decomposition for the β-$ROCH_2CH_2Cbl$'s were determined to be aquocobalamin (by UV–visible spectroscopy and HPLC retention), ethylene, and the alcohol, ROH (by GC/MS). Second-order rate constants have been determined for the base-on and base-off species of the β-$ROCH_2CH_2Cbl$'s as well as for the α-$ROCH_2CH_2Cbl$'s and the α- and β-$ROCH_2CH_2Cbi$'s. The reactivity is significantly dependent on the nature of R and varies by about 40-fold across each series of (alkoxyethyl)cobalt corrinoids. In addition, the base-on species of the β-$ROCH_2CH_2Cbl$'s are found to be 43- to almost 100-fold more reactive than the base-off species. Unlike the analogous cobaloximes in which the acid-induced decomposition is known to proceed via a σ-bonded ethylcobaloxime carbonium ion intermediate, no evidence of any kind could be found for the presence of an intermediate in the acid-induced decomposition of the (alkoxyethyl)cobalt corrinoids. The simplest mechanism which accounts for the data is thus a concerted elimination of the alcohol and the dealkylated cobalt corrinoid from the β-oxygen-protonated species, $RO(H)CH_2CH_2CoC^+$.

## Introduction

There remains much interest in the mechanisms of reactions in which carbon–cobalt bonds of organocobalt complexes are cleaved. One such prototypical reaction is the thermal- and acid-induced decomposition of organocobalt species containing a β-oxygen substituent in the organic ligand. Examples of this reactivity include the acid-induced and the heterolytic component of the ther-

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