Table II. Reaction of 2-Lithio-2-[(trimethylsilyl)ethynyl]-1,3-dithiane with Electrophiles (Y$^+$)

Y$^+$	product 5b; Y	% yield
H$_2$O	H	>90
D$_2$O	D	>90
CH$_3$I	CH$_3$	>90
Me$_3$SiCl	SiMe$_3$	98
		67
		72
		78
		92
	cis/trans 1:1 cis/trans 1:1	53

of dry *n*-Bu$_4$NF/THF in C$_6$D$_6$ with no electrophile, the isomerization to **6** (X = Y = Me$_3$Si) can be observed by NMR (ratio of **5b**/**6** ≤ 1:9). Unfortunately the lability of the allenes (**6**) has precluded their isolation and complete characterization to date.

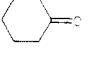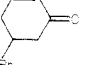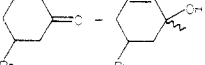The reactivity sequence of species **4e** was probed by partial alkylation. It would appear that initial reaction of this "dianion" occurs at the α-carbon: treatment with 1 equiv of MeI followed by a water quench affords **5a** (Y = Me) in >85% yield (GC). γ selective reaction without allene formation can be achieved through the stoichiometric γ-lithio derivative or by kinetic control, as illustrated by the product distributions given in Table I. In each case a THF solution of (Me$_3$Si)$_2$NLi containing a 2-fold excess of (Me$_3$Si)$_2$NH was added to a stirred mixture of dithiane **2a** and excess MeI in THF at −20 °C. After 30 min the product ratios were determined (by GC and/or NMR) after an aqueous quench.

Although the use of dianion **4e** alleviates the difficulties with allene formation inherent with anion **2e**, we have found γ-silyl derivative **2b** the most effective synthetically and the most readily available. Conversion of 3-(trimethylsilyl)propynal (**1b**)[9] to the corresponding dithiane (**2b**), mp 46–48 °C, occurs in acceptable yield (70–80%) under typical thioacetalization procedures.[4] Dithiane **2b** undergoes rapid and stoichiometric transmetalation in the presence of *n*-BuLi, *i*-Pr$_2$NLi, (Me$_3$Si)$_2$NLi, or C$_6$H$_5$CH$_2$-NHLi in THF solution. The acidity of **2b** is comparable to aniline in THF solution when lithium is the counterion (eq 2). This observation places dithiane **2b** at ca. 23 on our "pK_a" scale.[8]

The lithio species **4b** reacts with a variety of electrophiles (H$_2$O, D$_2$O, Me$_3$SiCl, MeI, allyl chlorides,[3] R$_2$CO, and RCHO; see Table II) to produce ethynyl (**5b**) rather than allenyl (**6b**) products in fair to excellent isolated yields. Aromatic and aliphatic aldehydes and aliphatic ketones
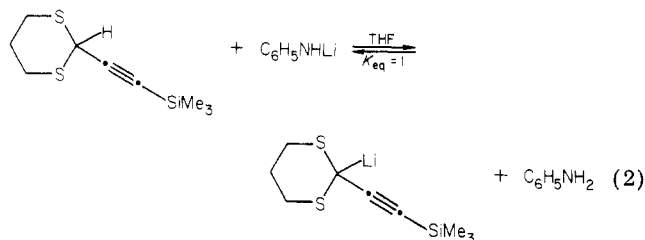
are equally acceptable as electrophiles. It is interesting to note (Table I) the complete lack of regio- and stereoselectivity in reaction with 5-phenyl-2-cyclohexenone. Amide-catalyzed desilylation is not a drawback in synthetic applications; e.g., **2b** shows no detectable desilylation in the presence of C$_6$H$_5$CH$_2$NLi/C$_6$H$_5$CH$_2$NH$_2$/THF after 43 h at −20 °C—and thus lithium or potassium amide solutions can be used to generate anion **4b** for synthetic applications.

Although preliminary studies indicate that selective α-alkylation can be expected when dianion **4e** is reacted with limited quantities of electrophiles, at present the γ-silyl derivative appears the superior reagent for this sequence (**2b** → **4b** → **5b**). Ethynyldithiane derivatives should prove useful in the synthesis of olefinic and allenic natural products; such studies are in progress.

Niels H. Andersen,* Alan D. Denniston
David A. McCrae

Department of Chemistry
University of Washington
Seattle, Washington 98195
Received September 30, 1981

(9) Prepared by oxidation of 3-(trimethylsilyl)propyn-1-ol[11] in 50–60% yield. See also: A. N. V. Komarov, O. G. Yarosh, and L. N. Astaf'eva, *Zh. Obsch. Khim.,* **36,** 907 (1966), from lithium (trimethylsilyl)acetylide and DMF; V. Jaeger, *Methoden Org. Chim. (Houben-Weyl),* 329 (1977).
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Δ$^{4,4'}$-4-Telluropyranyl-4H-telluropyrans. 1. Tellurosulfides and Tellurium–Sulfur Exchange

Summary: Δ$^{4,4'}$-2,2',6,6'-Tetraphenyl-4-telluropyranyl-4H-telluropyran and Δ$^{4,4'}$-7,7'-dimethoxy-2,2'-diphenyl-4-(benzo[*b*]telluropyranyl)-4H-benzo[*b*]telluropyran were prepared from the corresponding 4H-telluropyran-4-thiones and copper powder in refluxing toluene and re-

Scheme I
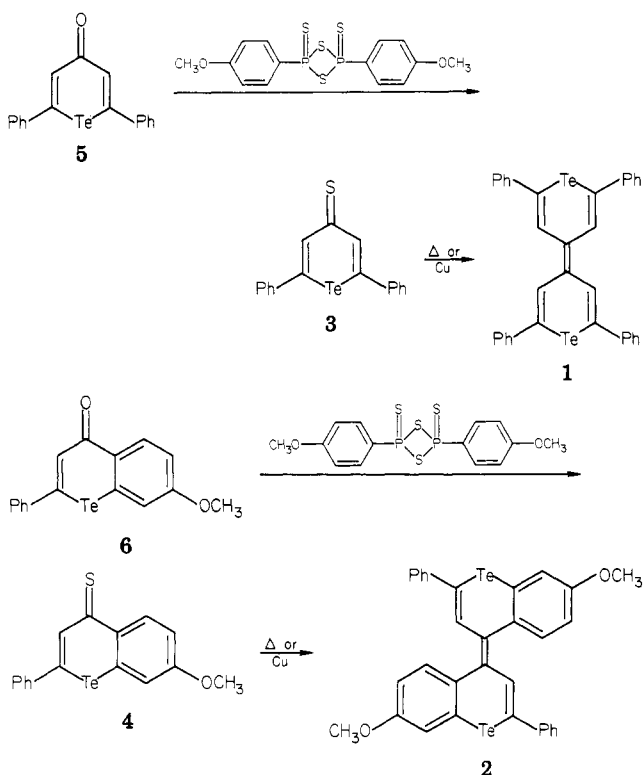
fluxing xylene, respectively, and were found to undergo facile tellurium–sulfur exchange.

Sir: Tellurium has been rediscovered by organic chemists as an anomalous element compared to the other chalcogens.[1] One reaction of organotellurium compounds that has been recognized since the beginning of this century is the facile replacement of tellurium by sulfur when an organotellurium compound is heated with sulfur. The exchange has been documented for bis(trialkylsilyl) tellurides,[2] diaryl tellurides,[3] phenoxtellurines,[4] and dibenzotellurophenes.[5] In certain cases, tellurium–selenium exchange has also been observed.[6] The mechanism of the exchange is unclear. We report here a novel tellurium–sulfur exchange as well as a stable sulfur analogue of a telluroxide in which tellurium has been oxidized by sulfur. These reactions occurred during the preparation of the first tellurium analogues of the bipyranylidene dimers, $\Delta^{4,4'}$-2,2′,6,6′-tetraphenyl-4-telluropyranyl-4*H*-telluropyran (1) and $\Delta^{4,4'}$-7,7′-dimethoxy-2,2′-diphenyl-4-(benzo[*b*]telluropyranyl)-4*H*-benzo[*b*]telluropyran (2).

In view of recent interest in the donor properties of the selenium analogue of tetrathiafulvalene[7] and the sulfur and selenium analogues of bipyranylidene-type dimers,[8] 1 and 2 would be of considerable interest as tellurium-containing donor molecules. We sought to prepare both 1 and 2 from the corresponding thiones 3 and 4 through a thermal- or metal-assisted dimerization with extrusion of sulfur (Scheme I).

Thione 3[9] was prepared in essentially quantitative yield by treating 2,6-diphenyl-4*H*-telluropyran-4-one (5)[10] with an excess of the Lawesson reagent[11] in hot toluene. When a xylene solution of 3 was warmed at reflux for 3 h, an insoluble, high-melting, metallic green solid precipitated that contained 1% or less of 1 according to field-desorption mass spectral data. The bulk of the product mixture was a 45:55 mixture of $\Delta^{4,4'}$-2,2′,6,6′-tetraphenyl-4-thiopyranyl-4*H*-thiopyran (7)[9] and the mixed tellurium–sulfur bipyranylidene 8.[9,12]

The addition of copper powder to the hot xylene solution of 3 increased the proportion of 1 in the product mixture, but significant amounts of both 7 and 8 remained (~5% each). Pure 1[9] was obtained in 66% yield by warming 3 with an equal weight of copper powder for 2 h in refluxing toluene. The product was easily removed from unreacted 3 by filtering 1 from a boiling acetonitrile solution of the soluble organics. Longer reaction times gave detectable amounts of 7 and 8.

A mixture of 1 and a 10-equiv excess of sulfur was stirred for 3 h in refluxing xylene; when the mixture cooled, 7 was obtained in 96% yield. Tellurium metal was the only other product detected. Attempts to produce 8 preferentially by control of the amount of sulfur or the reaction time failed in that 7 appeared to form nearly as rapidly as 8 in the early stages of exchange.

Thione 4 was isolated in 73% yield when 7-methoxy-2-phenyl-4*H*-benzo[*b*]telluropyran-4-one (6) was treated with the Lawesson reagent.[11] The dimer 2 was isolated in 12% yield from the reaction of 4 with copper powder in hot xylene. Very little (~2%) tellurium–sulfur exchange was indicated by field-desorption mass spectral data.

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(9) For 1: mp 273–274 °C; IR (KBr) 1590, 1490, 1440, 1230, 940, 850, 753, 690 cm⁻¹; UV λ_{max} (CH₂Cl₂) 520 nm (log ε 4.64); mass spectrum, *m/e* 692 (C₃₄H₂₄¹³⁰Te₂). Anal. Calcd for C₃₄H₂₄Te₂: C, 59.4; H, 3.5. Found: C, 59.4; H, 3.3. For 2: mp 266–268 °C; IR (KBr) 1587, 1550, 1475, 1290, 1250, 1225, 1035, 757, 693 cm⁻¹; UV λ_{max} (CH₂Cl₂) 410 nm (log ε 4.23); mass spectrum, *m/e* 700 (C₃₂H₂₄O₂¹³⁰Te₂). Anal. Calcd for C₃₂H₂₄O₂Te₂: C, 55.2; H, 3.5; Te, 36.7. Found: C, 54.6; H, 3.3; Te, 36.3. For 3: mp 120–123 °C (softens and dimerizes); ¹H NMR (90 MHz, CDCl₃) δ 8.23 (s, 2 H), 7.47 (m, 10 H); IR (KBr) 1545, 1480, 1068, 756, 690 cm⁻¹; mass spectrum, *m/e* 378 (C₁₇H₁₂S¹³⁰Te). Anal. Calcd for C₁₇H₁₂STe: C, 54.3; H, 3.2. Found: C, 54.2; H, 3.2. For 4: mp 136.5–138.5 °C; ¹H NMR (CDCl₃) δ 9.07 (d, 1 H, *J* = 9 Hz), 8.47 (s, 1 H), 7.30 (m, 5 H), 7.07 (d, 1 H, *J* = 2.5 Hz), 6.85 (dd, 1 H, *J* = 2.5, 9 Hz), 3.77 (s, 3 H); IR (KBr) 1590, 1485, 1332, 1115 cm⁻¹; mass spectrum, *m/e* 382 (C₁₆H₁₂OS¹³⁰Te). Anal. Calcd for C₁₆H₁₂OSTe: C, 50.6; H, 3.2. Found: C, 50.6; H, 2.9; S, 8.0; Te, 33.4. For 7: mp 318–320 °C (lit.[8d] mp 322–324 °C); UV λ_{max} (CH₂Cl₂) 474 nm; mass spectrum, *m/e* 496 (C₃₄H₂₄S₂). For 8: UV λ_{max} (CH₂Cl₂) 481 nm; mass spectrum, *m/e* 594 (C₃₄H₂₄S¹³⁰Te). For 9: ¹H NMR (CDCl₃) δ 9.10 (d, 1 H, *J* = 9 Hz), 8.25 (s, 1 H), 7.0–7.8 (m, 7 H), 6.73 (dd, 1 H, *J* = 2, 9 Hz), 3.95 (s, 3 H); UV λ_{max} (CH₂Cl₂) 450 nm (log ε 4.13); mass spectrum, *m/e* 284 (C₁₆H₁₂OS₂). For 10: mp 153.5–155 °C; ¹H NMR (Me₂SO-*d₆*) δ 8.90 (s, 1 H), 8.60 (d, 1 H, *J* = 9 Hz), 7.90 (m, 3 H), 7.40 (m, 3 H), 7.03 (dd, 1 H, *J* = 2.5, 9 Hz), 3.89 (s, 3 H); IR (KBr) 1590, 1465, 1225 cm⁻¹; UV λ_{max} (CH₂Cl₂) 582 (log ε 3.84), 680 nm (2.85); mass spectrum, *m/e* 414 (C₁₆H₁₂OS₂¹³⁰Te). Anal. Calcd for C₁₆H₁₂OS₂Te: C, 46.6; H, 2.9; S, 15.6. Found: C, 46.4; H, 3.1; S, 15.4.

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(12) Anal. Calcd for C₃₄H₂₄S₁.₄₅Te₀.₅₅: C, 76.8; H, 4.6; S, 8.7; Te, 13.2. Found: C, 76.7; H, 4.5; S, 8.8; Te, 12.4.

Scheme II

When **2** was treated with 5 equiv of sulfur in refluxing xylene for 2 h, **2** was completely consumed. Several products were detected by preparative thin-layer chromatography on silica gel eluted with methylene chloride, but only thione **9** was isolated in sufficient yield (70%) for characterization. Not only had tellurium–sulfur exchange occurred, but the bipyranylidene structure had reverted to the thione **9**.[9] The susceptibility of bipyranylidenes to add sulfur and revert to thiones has been observed.[14] The addition of triphenylphosphine to remove sulfur in the refluxing xylene/copper powder preparation of **2** improved the isolated yield of **2** to 32%.

A second product was isolated in low yield (24%) when **6** was treated with 2 mol equiv of the Lawesson reagent in benzene at room temperature for 17 h. This product was a sharp-melting (153.5–155 °C), purple-black solid that was insoluble in most solvents but moved with the solvent front on silica gel eluted with methylene chloride. The mass spectral and elemental analyses were consistent with a molecular formula of $C_{16}H_{12}OS_2Te$. The absorption spectrum with maxima (log ϵ) at 582 (3.84) and 680 nm (2.85) suggested a conjugated chromophore. The ^1H NMR spectrum displayed a one-proton singlet at δ 8.90.[9] The spectral and analytical data are consistent with structure **10**.[9]
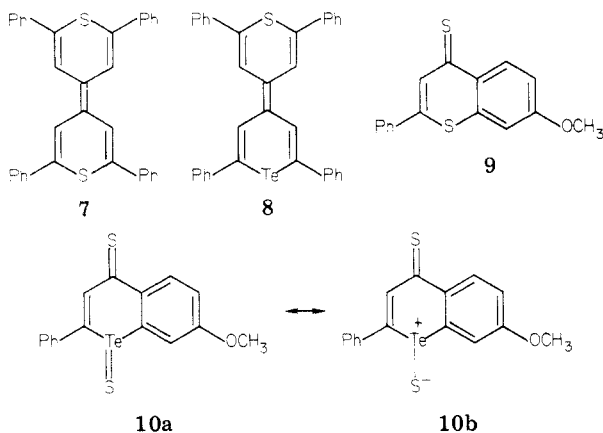
The tellurosulfide **10** represents the first stable member of its class. In this particular example, tellurium has been "oxidized" directly by sulfur, presumably from the Lawesson reagent. The resonance forms for such a structure are many; however, resonance form **10b** helps to rationalize the deshielding of the olefinic proton in **10** relative to the same proton in **4**.

When a toluene solution of **10** was warmed at reflux for 3 h, at least seven new products were formed. The major component, isolated in 20% yield, was identified as thione **9** by ^1H NMR and field-desorption mass spectroscopy.

It is conceivable that elemental sulfur might act as an oxidant under suitable conditions. As shown in Scheme II, electron transfer from tellurium to elemental sulfur at elevated temperature might give a radical cation/radical anion pair which could then collapse to produce the tellurosulfide. As the oxidation potentials in Table I indicate, both **1** and **2** are easily oxidized with $E^{o'}_{oxid}$ for **1** being +0.34

Table I. Oxidation Potentials of 1 and 2

		oxidation potential,[a] V			
		I		II	
compd	electrode	forward	reverse	forward	reverse
1	platinum	+0.37	+0.30	+0.52	+0.45
	glassy carbon	+0.39	+0.28	+0.54	+0.43
2	platinum	+0.44[b]	+0.34[c]		
	glassy carbon	+0.43[b]	+0.33[c]		

[a] Relative to standard calomel electrode (saturated aqueous NaCl) with CH_2Cl_2 as solvent with 0.1 M tetra-*n*-butylammonium tetrafluoroborate as supporting electrolyte. [b] Two-electron oxidation. [c] Adsorbed.

V (average of forward and reverse) and $E^{o'}_{oxid}$ for **2** being $\sim$+0.39 V. Both **1** and **2** should be fair reducing agents. The Lawesson reagent could serve as a source of sulfur to produce tellurosulfide **10**.

The tellurium–sulfur exhange observed upon heating **10** suggests that tellurosulfide species may be involved as intermediates. We are presently seeking other stable tellurosulfides. The donor properties of both **1** and **2** and other tellurobipyranylidenes as well as their conductive salts will be reported in a separate paper.

Michael R. Detty,* **Bruce J. Murray**

Research Laboratories
Eastman Kodak Company
Rochester, New York 14650
Received October 22, 1981

A Convergent Total Synthesis of Methoxatin

Summary: We report a convergent total synthesis of the coenzyme methoxatin (**1**) by linking pyrrole subunit (**3**) with uvitonic acid derivative **4d** and oxidative photocyclization to deoxymethoxatin triester **6**, followed by seven refunctionalization steps to **1**.

Sir: A number of bacteria, known as methylotrophs, can utilize methanol as their sole carbon source. The organisms, of which *Pseudomonas* are typical, are of current interest as nutritive single-cell protein. The oxidation of methanol to formaldehyde and to formic acid is accomplished in these organisms by a methanol dehydrogenase which utilizes a newly discovered coenzyme, methoxatin (**1**),[1] quite different in structure from the familiar redox coenzymes such as flavin, nicotinamide, etc. The structure of methoxatin was deduced from spectroscopic data[2,3] and an X-ray crystallographic study[4] of its aldol adduct with acetone (**2**), but continued studies of its mode of action have been severely hampered by lack of adequate quantities of the natural coenzyme (**1**).

In keeping with our recent analysis[5] we conceived a convergent synthesis of methoxatin from appropriate pyridine and pyrrole starting materials, to be linked and

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