Organometallics 1988, *7*, 84–87

Acetylenic Tellurides: Synthesis and Reactivity

Miguel J. Dabdoub and João V. Comasseto*

Instituto de Quimica, Universidade de São Paulo, Caixa Postal, 20780-01498 São Paulo, Brasil

Received April 30, 1987

Acetylenic tellurides were prepared by the reaction of lithium phenylacetylide with (*p*-methoxyphenyl)tellurium bromide or with elemental tellurium, followed by alkylation of the intermediate lithium phenylacetylenetellurolate with primary or secondary alkyl halides. The acetylenic tellurides can function as either nucleophilic or electrophilic tellurium centers. Reaction of these intermediates with reducing agents, followed by air oxidation, gives dialkyl ditellurides in high yields, along with the tellurium-free phenylacetylene. Reaction of these intermediates with reducing agents under nitrogen, followed by reaction with alkyl halides, furnishes symmetrical and unsymmetrical dialkyl tellurides in high yields. The reaction of acetylenic tellurides with alkyl Grignard or alkyllithium reagents led to the formation of symmetrical or unsymmetrical dialkyl tellurides in good yields.

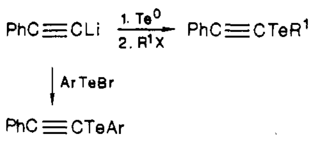
Introduction

Acetylenic sulfides and the corresponding sulfones[1] as well as acetylenic selenides[2] are acquiring increasing importance as synthetic tools. Although organotellurium compounds have attracted considerable interest as reagents and intermediates in organic synthesis during the last few years,[3] acetylenic tellurides have been studied little. To our knowledge, only the hydrolysis of (methyltelluro)-phenylacetylene by mercuric salts in acidic medium to give a mixture of acetophenone and phenylacetylene,[4] the transformation of chloromethyl(telluro)alkynes into 1,3-ditellurole, when treated with Li_2Te in ethanol,[5] and the protonation of sodium phenylacetylenetellurolate with hydrogen chloride[6] or trifluoroacetic acid[7] to give cyclic tellurium species have thus far been reported in the literature.

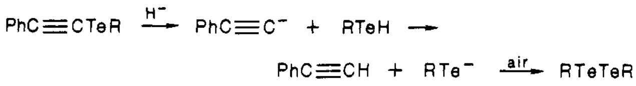
Preliminary results about the Te–sp C bond cleavage in acetylenic tellurides, using reducing agents, have been recently reported by us.[8] In this paper we report a study of the properties of these compounds as electrophilic or nucleophilic tellurium reagents.

Diorganyl ditellurides and tellurides are important reagents in organic synthesis[3,9] and constitute starting materials for the preparation of other classes of organic tellurium compounds.[3] The more common approach to the synthesis of dialkyl ditellurides and tellurides is based on the alkylation of disodium ditelluride or disodium telluride, respectively, which can be easily prepared from elemental tellurium and many reducing agents.[10] Control of the tellurium/reducing agent ratio permits us to obtain, selectively, the telluride or ditelluride, but this methodology is inconvenient in that the anions are unstable in air and must be prepared and used "in situ". Unsymmetrical dialkyl tellurides cannot be prepared directly by the alkylation of disodium telluride. However, methods are available that employ diorganyl ditellurides as starting materials in the synthesis of unsymmetrical tellurides.[11]

Scheme I



Scheme II



In this paper we describe a new and general method of obtaining dialkyl ditellurides and symmetrical as well as unsymmetrical dialkyl tellurides, using acetylenic tellurides as the starting materials.

Results and Discussion

The acetylenic tellurides can be prepared by the reaction of the lithium acetylide with tellurium, followed by trapping the intermediate lithium tellurolates with alkyl halides, or by the reaction of the corresponding lithium acetylide in tetrahydrofuran at 0 °C under nitrogen with aryltellurium bromides generated "in situ" (Scheme I; Table I). The latter are prepared by the reaction between diaryl ditellurides and bromine.[12] In both cases the acetylenic tellurides are obtained in excellent yields.

The stability of the product depends on the nature of the organic group linked to tellurium. The aromatic and primary aliphatic derivatives are stable compounds, but prolonged exposure to light and atmosphere should be avoided to prevent oxidation or decomposition. When a secondary aliphatic group is linked to tellurium, the compound is less stable but can be stored for several months in the dark under refrigeration. Under these conditions only negligible deposition of tellurium is observed.

---

(1) a) Braga, A. L.; Comasseto, J. V.; Petragnani, N. *Tetrahedron Lett.* **1984**, *25*, 1111. (b) Eisch, J. J.; Behrooz, M.; Colle, J. E. *Tetrahedron Lett.* **1984**, 25, 4851.

(2) Comasseto, J. V.; Catani, V.; Ferreira, J. T. B.; Braga, A. L. *J. Chem. Soc., Chem. Commun.* **1986**, 1067 and references therein.

(3) Petragnani, N.; Comasseto, J. V. *Synthesis 1986*, 1.

(4) Boiko, Y. A.; Kupin, B. S.; Petrov, A. A. *Zh. Org. Khim.* **1968**, *4*, 1335.

(5) Bender, S. L.; Detty, M. R.; Haley, N. F. *Tetrahedron Lett.* **1982**, 1531.

(6) Bender, S. L.; Haley, N. F.; Luss, H. R. *Tetrahedron Lett.* **1981**, 1495.

(7) Lakshmikantham, M. V.; Cava, M. P.; Albeck, M.; Engman, L.; Wudl, F.; Aharon-Shalom, E. *J. Chem. Soc., Chem. Commun.* **1981**, 828.

(8) Dabdoub, M. J.; Dabdoub, V. B.; Comasseto, J. V.; Petragnani, N. *J. Organomet. Chem.* **1986**, *308*, 211; **1986**, *317*, C33.

(9) Suzuki, H.; Hanazaki, Y. *Chem. Lett.* **1986**, 549.

(10) For a review see: Petragnani, N.; Comasseto, J. V. *Proceedings of the Fourth International Conference on Organic Chemistry of Selenium and Tellurium*; The University of Aston, Birmingham, England, 1983; pp 98–241.

(11) a) Petragnani, N. *Chem. Ber* **1963**, *96*, 247. b) Okamoto, J.; Iano, T. *J. Organomet. Chem.* **1971**, *29*, 99. (c) Piette, J. L.; Renson, M. *Bull. Soc. Chim. Belg.* **1970**, *79*, 253. d) Ibid. **1970**, *79*, 367. (e) *Ibid.* **1971**, *80*, 669. (f) Irgolic, K.; Busse, P. J.; Grigsby, R. A. *J. Organomet. Chem.* **1975**, *88*, 175. (g) Goodman, M. M.; Knapp, F. F. *J. Org. Chem.* **1982**, *47*, 3004. h) Grigsby, R. A.; Irgolic, K.; Knapp, F. F.; *J. Organomet. Chem.* **1983**, *253*, 31. (i) Comasseto, J. V.; Ferreira, J. T. B.; Fontanillas Val, J. A. *J. Organomet. Chem.* **1984**, *277*, 261. (j) Ferreira, J. T. B.; Simonelli, F.; Comasseto, J. V. *Synth. Commun.* **1986**, *16*, 1335. For a review see ref 10.

(12) Petragnani, N.; Torres, L.; Wynne, K. J. *J. Organomet. Chem.* **1975**, *92*, 185.

0276-7333/88/2307-0084$01.50/0 © 1988 American Chemical Society

Table I. Phenyl(organyltelluro)acetylenes Prepared

compd	yield, %	IR, cm^{-1}	^1H NMR, ppm (*J*, Hz)[d]	anal. found (calcd) H	anal. found (calcd) C
$PhC{\equiv}CTeC_4H_9$[a]	97	2.130 (m)	0.95 (t, *J* = 7, 3 H), 1.1–2.2 (m, 4 H), 2.90 (t, *J* = 7, 2 H), 7.33 (m, 6 H)	4.98 (4.90)	50.26 (50.42)
$PhC{\equiv}CTeC_{12}H_{25}$[a]	90	2.132 (m)	0.88 (m, 3 H), 1.0–1.6 (m, 18 H), 1.93 (t, *J* = 7, 2 H), 2.88 (t, *J* = 7, 2 H), 7.31 (m, 6 H)	7.63 (7.54)	60.38 (60.36)
$PhC{\equiv}CTeCH_2CH_2Ph$[b]	91	2.125 (m)	3.18 (m, 4 H), 7.1–7.4 (m, 12 H)	4.36 (4.19)	57.76 (57.55)
$PhC{\equiv}CTeCH(CH_3)_2$[a]	95	2.130 (m)	1.75 (d, *J* = 7, 6 H), 3.56 (sext, *J* = 7, 1 H), 7.3 (m, 6 H)	4.63 (4.41)	48.48 (48.60)
$PhC{\equiv}CTeCH(CH_3)CH_2CH_2CH_3$[a]	96	2.130 (m)	0.96 (t, *J* = 7, 3 H), 1.1–2.1 (m, 4 H), 1.81 (d, *J* = 7, 3 H), 3.53 (sext, *J* = 7, 1 H), 7.33 (m, 6 H)	5.14 (5.34)	51.86 (52.06)
$PhC{\equiv}CTe(p\text{-}CH_3OC_6H_4)$[c]	73		3.7 (s, 3 H), 6.79 (d, *J* = 9, 2 H); 7.3 (m, 5 H), 7.71 (d, *J* = 9, 2 H)	3.72 (3.57)	53.4 (53.63)
$PhC{\equiv}CTeC_2H_5$[a]	95	2.130 (m)	1.8 (t, *J* = 7, 3 H), 2.81 (q, *J* = 7, 2 H), 7.23 (m, 5 H)	3.92 (3.88)	46.53 (46.58)

[a] Yellow liquid purified by column chromatography using hexane as eluent. [b] Yellow solid recrystallized from ethanol; mp 42–43 °C. [c] Yellow solid recrystallized from ethanol; mp 71–72 °C. [d] TMS internal standard.

Table II. Diorganyl Ditellurides Prepared

ditelluride	yield, %	^1H NMR, ppm (*J*, Hz)[h]	anal. found (calcd) H	anal. found (calcd) C
$(n\text{-}C_{12}H_{25}Te)_2$[d,g]	95,[a] 86[b]	0.88 (m, 6 H), 1.1–2.1 (m, 40 H), 3.11 (t, *J* = 7, 4 H)	8.47 (8.42)	48.86 (48.55)
$(n\text{-}C_4H_9Te)_2$[f,g]	96,[a] 92,[b] 73[c]	0.93 (t, *J* = 7, 6 H), 1.1–1.9 (m, 8 H), 3.11 (t, *J* = 7, 4 H)	4.87 (4.89)	25.95 (26.00)
$(n\text{-}C_2H_5Te)_2$[f]	91,[b] 70[c]	1.65 (t, *J* = 7, 6 H), 3.05 (q, *J* = 7, 4 H)	22	
$(PhCH_2CH_2Te)_2$[f]	92[a]	2.8–3.4 (m, 8 H), 7.18 (s, 12 H)	3.9 (3.87)	41.61 (41.27)
$((CH_3)_2CHTe)_2$[f]	91[a]	1.63 (d, *J* = 7, 12 H), 3.45 (hept, *J* = 7, 2 H)	23	
$(CH_3CH_2CH_2CH(CH_3)\text{-}Te)_2$[f]	87[a]	0.7–1.1 (m, 6 H), 1.1–1.9 (m, 8 H), 1.63 (d, *J* = 7, 6 H), 2.9–3.6 (m, 2 H)	5.36 (5.53)	30.19 (30.21)
$(p\text{-}CH_3OC_6H_4Te)_2$[e]	95,[a] 93[b]	3.73 (s, 6 H), 6.6 (d, *J* = 9, 4 H), 7.56 (d, *J* = 9, 4 H)	20	

[a] $NaBH_4$/ethanol. [b] $LiAlH_4$/THF. [c] N_2H_4/OH^-. [d] Recrystallized from ethanol, mp 43–44 °C. [e] Recrystallized from ether; mp 57–58 °C. [f] Dark red liquids purified by filtration through a silica gel column under pressure eluting with hexane or ether. [g] These compounds were prepared on a 50-mmol scale. A 1-L round-bottom flask must be used when the reduction was made with $NaBH_4$/EtOH (50 mL), due to the abundant foam formation. Reduction with $LiAlH_4$/THF (50 mL) must be performed at 0 °C since the reaction is exothermic. [h] TMS Internal Standard.

We have tried to reduce the acetylenic tellurides to the corresponding vinylic tellurides, in a manner analagous to the known reduction of acetylenic selenides.[13] Many reducing agents were used, such as $LiAlH_4$ in tetrahydrofuran and $NaBH_4$ in ethanol, but the only products obtained were the tellurium-free acetylene and the diorganyl ditelluride in high yields (eq 1; Table II).

$$PhC{\equiv}CTeR \xrightarrow[2.\ [O]]{1.\ [H]} PhC{\equiv}CH + RTeTeR \tag{1}$$

The reduction of acetylenic tellurides with hydrazine–sodium hydroxide (diimide) leads to the formation of a mixture of diorganyl ditellurides (70–73%) and vinylic tellurides of cis configuration (8–14%). The products were separated by column flash chromatography.

Reduction with $NaBH_4$ and $LiAlH_4$ is presumed to occur through attack of hydride at the tellurium atom, generating a tellurol and an acetylide anion. This assumption is based on the appearance of a dark red color after the addition of the reducing agent. In most cases this red color disappears spontaneously[14] with vigorous gas evolution to give a colorless solution presumed to be a mixture of the acetylene and the tellurolate anion. In some cases (e.g., (dodecyltelluro)phenylacetylene) slight warming is necessary before gases are evolved. The tellurolate anion intermediate is oxidized by air to give the corresponding diorganyl ditelluride (Scheme II); when the reaction was run with $NaBH_4$ at 0 °C, gas evolution was not observed and the tellurol was oxidized directly to the corresponding ditelluride.

Table III. Vinylic Tellurides Obtained

compd	yield, %	IR	^1H NMR, ppm (*J*, Hz)[c]
$PhCH{=}CHTeC_4H_9$	93,[a] 14[b]	1590 (m), 755 (s)	0.93 (t, *J* = 7, 3 H), 1.1–2.1 (m, 4 H), 2.76 (t, *J* = 7, 2 H), 7.00 (d, *J* = 11, 1 H), 7.33 (s, 5 H), 7.44 (d, *J* = 11, 1 H)
$PhCH{=}CHTeC_{12}H_{25}$	80[a]	1595 (m), 760 (s)	0.7–1.0 (m, 3 H), 1.0–2.0 (m, 20 H), 2.63 (t, *J* = 7, 2 H), 6.80 (d, *J* = 11, 1 H), 7.2 (s, 5 H), 7.26 (d, *J* = 11, 1 H)
$PhCH{=}CHTeC_2H_5$	8[b]		1.58 (t, *J* = 7, 3 H), 2.53 (q, *J* = 7, 2 H), 6.61 (d, *J* = 11, 1 H), 6.95 (s, 5 H), 7.05 (d, *J* = 11, 1 H)

[a] $NaBH_4$/ethanol under reflux. [b] N_2H_4/OH^- at room temperature (by product of the reduction of the corresponding acetylenic tellurides to dialkyl ditellurides). [c] TMS internal standard.

The intermediacy of the tellurolate anion in this sequence was confirmed by performing the reaction under

---

[13] Comasseto, J. V.; Ferreira, J. T. B.; Petragnani, N. *J. Organomet. Chem.* **1981**, *287*, 216.

[14] After 25–30 min, when $NaBH_4$ in ethanol is used and instantaneously with $LiAlH_4$ in tetrahydrofuran.

Table IV. Dialkyl Tellurides ($RTeR^1$) Prepared

R	R^1X or R^1M	reactn time, min	yield, %	^1H NMR, ppm (*J*, Hz)[b]	anal. found (calcd)	
					H	C
$n\text{-}C_{12}H_{25}$	$n\text{-}C_{12}H_{25}Br$	30	87	0.88 (m, 6 H), 1.1–1.9 (m, 40 H), 2.65 (t, $J = 7$, 4 H)	10.79 (10.73)	61.94 (61.85)
$n\text{-}C_4H_9$	$n\text{-}C_4H_9Br$	10	89	0.91 (t, $J = 7$, 6 H), 1.1–1.9 (m, 8 H), 2.61 (t, $J = 7$, 6 H)	24	
	$n\text{-}C_4H_9Li$	10	93			
$n\text{-}C_4H_9$	$PhCH_2CH_2Br$	15	84	0.88 (t, $J = 7$, 3 H); 1.1–1.9 (m, 4 H), 2.58 (t, $J = 7$, 2 H); 2.7–3.2 (m, 4 H), 7.18 (s, 6 H)	6.43 (6.21)	49.72 (49.74)
$PhCH_2CH_2$	$n\text{-}C_{12}H_{25}Br$	25	83	0.88 (m, 3 H), 1.1–1.9 (m, 20 H), 2.60 (t, $J = 7$, 2 H), 2.8–3.2 (m, 4 H), 7.23 (s, 6 H)	8.54 (8.46)	60.10 (59.76)
$(CH_3)_2CH$	$n\text{-}C_{12}H_{25}Br$	30	88	0.88 (m, 3 H), 1.1–2.0 (m, 20 H), 1.6 (d, $J = 7$, 6 H), 2.68 (t, $J = 7$, 2 H), 3.36 (hept, $J = 7$, 1 H)	9.04 (9.42)	53.21 (53.00)
	$n\text{-}C_{12}H_{25}MgBr$	30	68			
$n\text{-}C_{12}H_{25}$	$(CH_3)_2CHBr$	4 h	63			
$n\text{-}C_{12}H_{25}$	C_4H_9MgBr	30	71	0.8–1.8 (m, 30 H), 2.55 (t, $J = 7$, 4 H)	9.54 (9.61)	54.06 (54.29)
	C_4H_9Li	10	95			
$(CH_3)_2CH$	C_4H_9MgBr	30	67	0.91 (t, $J = 7$, 3 H), 1.56 (d, $J = 7$, 6 H), 1.1–1.9 (m, 4 H), 2.58 (t, $J = 7$, 2 H); 3.23 (hept, $J = 7$, 1 H)	*a*	

[a] The compound is unstable and undergo easy "air oxidation", giving a white solid. [b] TMS internal standard.

deoxygenated nitrogen, at reflux. In this way, nucleophilic addition of the tellurolate anion to phenylacetylene occurs, and vinylic tellurides could be obtained in high yields (eq 2, Table III). This reaction occurs only when sodium borohydride in ethanol is used because a protic solvent is necessary to capture the intermediate vinyl anion.

$$PhC{\equiv}CTeR \xrightarrow[N_2/\text{reflux}]{NaBH_4/\text{ethanol}} \underset{\text{cis}}{PhCH{=}CHTeR} \qquad (2)$$

Another conclusive result was obtained by the introduction of an alkylating agent into the reaction medium, under nitrogen. In this way symmetrical and unsymmetrical dialkyl tellurides were obtained in good yields (eq 3, Table IV).

$$PhC{\equiv}CTeR \xrightarrow[R^1X,\ \text{room temp}]{NaBH_4/\text{ethanol}/N_2} RTeR^1 + PhC{\equiv}CH \qquad (3)$$

The reaction with primary alkyl halides occurs rapidly (10–30 min); with isopropyl bromide the reaction is slower (4 h).

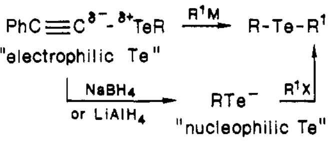
In addition to the theoretical interest in the field of the tellurium chemistry, these reactions have preparative importance when R and R^1 are aliphatic groups, since most methods for the preparation of dialkyl tellurides and ditellurides are not general.[10]

In most cases elemental tellurium fails to react with aliphatic Grignard reagents.[15] An isolated example of the reaction of tellurium with *tert*-butylmagnesium bromide in tetrahydrofuran/hexamethylphosphorus triamide was reported.[16] The insertion of tellurium into a lithium–sp^3 carbon bond of *n*-butyllithium and *tert*-butyllithium was described.[17] Therefore we took advantage of the easy insertion of tellurium into metal–sp carbon bonds to prepare dialkyl tellurides and ditellurides as described above. The whole process constitutes a formal insertion of tellurium into a metal–sp^3 carbon bond. On the other hand, the acetylenic moiety of the acetylenic telluride is not lost but can be quantitatively recovered by careful evaporation under vacuum.

Reaction of acetylenic tellurides with Grignard or organolithium reagents led to the cleavage of the tellurium–sp carbon bond with formation of a diorganyl telluride in good yield and the free acetylene (eq 4, Table IV).

$$PhC{\equiv}CTeR \xrightarrow[2.\ H_2O]{1.\ 2\ R^1MgX\ \text{or}\ R^1Li} PhC{\equiv}CH + RTeR^1 \qquad (4)$$

Scheme III



Two equivalents of the Grignard reagent were necessary to transform all of the acetylenic telluride into the diorganyl telluride; in the case of organolithium reagents 1 equiv is sufficient to complete the reaction.

In this case the acetylenic tellurides constitute a source of electrophilic tellurium. When these compounds react with a hydride, an inversion of polarity at tellurium occurs and the acetylenic tellurides constitute a source of nucleophilic tellurium, which makes them very versatile intermediates as shown in Scheme III.

Theoretically, the Te–sp^3 carbon bond is estimated to have 6% ionic character, since the difference in electronegativities between carbon and tellurium is 0.49.[18] The ease with which tellurium is attacked by nucleophiles and the specificity with which the tellurium–sp carbon bond is cleaved indicate that this bond is highly polarized. This can be attributed to the higher electronegativity of sp carbon compared with the sp^3 carbon, as well as to the low electronegativity of tellurium.[18] According to the considerations made above, acetylenic tellurides are similar in reactivity to the unstable organotellurium halides and cyanates.[19]

Experimental Section

General Data. ^1H NMR spectra were recorded on a Varian T-60 spectrometer; IR spectra, in the form of liquid films in NaCl, were measured with a Perkin-Elmer 457A spectrophotometer. All the alkyl halides and phenylacetylene were distilled prior to use. Merck silica gel 60 (70–230 mesh and 230–400 mesh) was used for column chromatography, and prepared plates (silica gel $60F_{254}$ on aluminum) were used for thin-layer chromatography. Melting points were determined in a Kofler hot plate and are uncorrected. Bis(*p*-methoxyphenyl) ditelluride was prepared according to published procedures.[20] The Grignard reagents used in this work were freshly prepared by reaction of the appropriate organic halide with magnesium in dry ether.[21] Tellurium of ca. 320 mesh from

---

(15) Haller, W.; Irgolic, K. J. *J. Organomet. Chem.* **1972**, *38*, 97.

(16) Jones, C. H. W.; Sharma, R. D. *J. Organomet. Chem.* **1983**, *255*, 61.

(17) Cava, M. P.; Engmann, L. *Synth. Commun.* **1982**, *12*, 163.

(18) Haiduc, I.; Zuckerman, J. *Basic Organometallic Chemistry*; Walter de Gruyter: Berlin, 1985.

(19) (a) Spencer, H. K.; Lakshmikantham, M. V.; Cava, M. P. *J. Am. Chem. Soc.* **1977**, *99*, 1470. (b) Wiriyachitra, P.; Faleone, S. J.; Cava, M. P. *J. Org. Chem.* **1979**, *44*, 3957. (c) Engmann, L.; Cava, M. P. *J. Org. Chem.* **1981**, *46*, 4194.

(20) Reichel, L.; Kirschbaum, E. *Chem. Ber.* **1943**, *76*, 115.

(21) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; Wiley: New York, 1967; p. 415.

(22) Mallet, J. W. *Justus Liebigs Ann. Chem.* **1851**, *79*, 223.

different suppliers was used. It was dried overnight at 110 °C prior to use.

Preparation of Phenyl(alkyltelluro)acetylenes. *n*-Butyllithium (22.2 mL, 30 mmol, 1.35 M solution in hexane) was added dropwise to a solution of phenylacetylene (3.10 g, 30.0 mmol) in THF (15 mL) at 0 °C under nitrogen. After 5 min of stirring at 0 °C elemental tellurium (3.90 g, 30.0 mmol) was added and the mixture was refluxed until the tellurium disappeared (~30 min). The heat source was removed, and the alkyl halide (30 mmol) was added. The mixture was stirred for 40 min at room temperature, then diluted with ether (60 mL), and washed with brine, and the organic layer was dried over magnesium sulfate. The solvents were evaporated, and the residue was purified by flash chromatography on silica gel eluting with hexane (for yields and physical data, see Table I).

Preparation of Phenyl[(*p*-methoxyphenyl)telluro]acetylene. To a solution of lithium phenylacetylide (20.0 mmol) prepared as described above was added dropwise a solution of (*p*-methoxyphenyl)tellurium bromide [prepared by adding bromine (1.60 g, 10.0 mmol) in benzene (5 mL) to a solution of bis(*p*-methoxyphenyl) ditelluride (4.69 g, 10 mmol) in THF (10 mL) at 0 °C under nitrogen]. The reaction mixture was stirred for 1 h at room temperature and then treated as described above to give solid phenyl[(*p*-methoxyphenyl)telluro]acetylene: yield 4.90 g (73%); mp 71–72 °C (recrystallized from ethanol).

Preparation of Diorganyl Ditellurides from Phenyl(organyltelluro)acetylenes (Reduction with $NaBH_4$). Sodium borohydride (0.081 g, 2.20 mmol) in ethanol (3.0 mL) was added to a solution of the acetylenic telluride (2.00 mmol) in ethanol (10 mL) at 0 °C (for primary) or at ~40–50 °C (for secondary). The pale yellow solution turned dark red. After the solution was stirred for 10 min at this temperature, water (0.5 mL) and a 10% solution of sodium hydroxide (0.5 mL) were added and the mixture was stirred at 0 °C for 10 min. The reaction mixture was diluted with ether (30 mL) and washed with brine, and the organic layer was dried over magnesium sulfate. The solvent was evaporated, and the phenylacetylene was cautiously evaporated at reduced pressure (collected in a trap at –78 °C). The evaporated residue yielded the pure diorganyl ditelluride in yields as reported in Table II.

Preparation of Dialkyl Tellurides from Phenyl(alkyltelluro)acetylenes (Reduction with $NaBH_4$ Followed by Alkylation). Sodium borohydride (0.081 g, 2.2 mmol) in ethanol (3.0 mL) was added to a solution of the phenyl(alkyltelluro)acetylene (2.0 mmol) and an alkyl halide (2.0 mmol) in ethanol (10 mL) at room temperature under a strong flow of nitrogen. The mixture was slightly warmed (~60–65 °C) until the red color turned pale yellow and gas evolution was observed (25–30 min). The mixture then was stirred at room temperature for a period of time as indicated on Table IV. The reaction was quenched with water (0.5 mL) and 10% sodium hydroxide solution (0.5 mL) and diluted with ether (30 mL). The mixture was washed with brine, the organic layer was dried over magnesium sulfate, and the solvent was removed by evaporation. The phenylacetylene was evaporated at reduced pressure (collected at –78 °C), and the residue was chromatographed on silica gel eluting with hexane to give the dialkyl tellurides with the yields reported on Table IV.

Preparation of Dialkyl Tellurides by the Reaction between Phenyl(alkyltelluro)acetylenes and Alkyl Grignard Reagents. A solution of the phenyl (alkyltelluro)acetylene (2 mmol) in ether (3 mL) was added dropwise to a solution of the Grignard reagent (4 mmol) in ether (5 mL) at room temperature under nitrogen. After 30 min of stirring at room temperature the mixture was washed with saturated ammonium chloride and the organic layer was dried over magnesium sulfate. The solvent was evaporated, and the residue was chromatographed on silica gel eluting with heptane to give the dialkyl tellurides with the yields reported on Table IV.

Preparation of Dialkyl Tellurides by the Reaction of Phenyl(alkyltelluro)acetylenes with Alkyllithium Reagents. *n*-Butyllithium (1.59 mL, 2.2 mmol, 1.38 M solution in hexane) was added dropwise to a solution of phenyl(alkyltelluro)acetylene (2 mmol) in THF (10 mL) at 0 °C under nitrogen. Following the addition, the solution was stirred for 10 min at this temperature, then brine was added, and the product was extracted with ether. The organic layer was dried over $MgSO_4$ and evaporated under reduced pressure. The dialkyl tellurides were obtained in yields as reported in Table IV.

Preparation of Vinylic Tellurides by the Reaction of Phenyl(alkyltelluro)acetylenes with Sodium Borohydride under Reflux. Sodium borohydride (0.093 g, 2.5 mmol) in ethanol (3.0 mL) was added to a solution of the phenyl(alkyltelluro)acetylene (2.0 mmol) in ethanol (10 mL) under nitrogen. The solution was stirred under reflux for 3 h (the red color turned pale yellow). The heating was terminated, and the pale yellow solution was treated with water (0.5 mL) and a 10% solution of sodium hydroxide (0.5 mL) and diluted with ether (30 mL). The mixture was washed with brine, the organic layer was dried over magnesium sulfate, and the solvent was evaporated. The residue was chromatographed on silica gel eluting with hexane to give the vinylic tellurides in yields as reported in Table III.

Diorganyl Ditellurides from Phenyl(organyltelluro)acetylenes (Reduction with $LiAlH_4$). To a suspension of $LiAlH_4$ (0.09 g, 2.2 mmol) in THF (3 mL) at room temperature was added a solution of the acetylenic telluride (2 mmol) in THF (10 mL). The mixture was stirred for 10 min, then water (0.5 mL), 10% sodium hydroxide solution (0.5 mL), and water (0.5 mL) were added, the mixture was diluted with ether, and the red solution was washed with brine. The organic layer was dried over magnessium sulfate, and the solvent and phenylacetylene were evaporated at reduced pressure. The residue remaining after evaporation gave the pure diorganyl ditelluride in yields as reported in Table II.

Diorganyl Ditellurides from Phenyl(alkyltelluro)acetylenes (Reduction with Hydrazine–NaOH (Diimide)). To a solution of the acetylenic telluride (2 mmol) in ethanol (8 mL) containing 0.3 g of solid NaOH were added three equal portions of 97% hydrazine (total 1.2 mL) at 10-min intervals. Following the last addition the mixture was stirred for 5 min. Water was then added, and the ethanol was removed under reduced pressure. The concentrated mixture was extracted with ether and washed with water. The organic layer was dried over $MgSO_4$, and the solvent was evaporated. The residue consisted of a mixture of the dialkyl ditelluride and vinylic telluride that were separated by flash chromatography using hexane as eluent in the yields reported in Tables II and III.

Acknowledgment. We acknowledge the following Brazilian Agencies for financial support: FAPESP, CAPES, CNPq, and FINEP. Acknowledgment is also made to Ms. Narimatzu for elemental analyses, to D.Q.-UFSCar for some MS spectra, and to Prof. R. Zingaro (Texas A&M University) for a generous gift of tellurium.

Registry No. Te, 13494-80-9; $PhC\equiv CH$, 536-74-3; C_4H_9Br, 109-65-9; $C_{12}H_{25}Br$, 143-15-7; $PhCH_2CH_2Br$, 103-63-9; $(CH_3)_2CHBr$, 75-26-3; $CH_3CH_2CH_2CH(CH_3)Br$, 107-81-3; $p\text{-}CH_3OC_6H_4Br$, 55843-72-6; C_2H_5Br, 74-96-4; $PhC\equiv CTeC_4H_9$, 105797-59-9; $PhC\equiv CTeC_{12}H_{25}$, 110615-15-1; $PhC\equiv CTeCH_2CH_2Ph$, 110615-16-2; $PhC\equiv CTeCH(CH_3)_2$, 110615-17-3; $PhC\equiv CTeCH(CH_3)CH_2CH_2CH_3$, 110615-18-4; $PhC\equiv CTe(p\text{-}CH_3OC_6H_4)$, 108162-22-7; $PhC\equiv CTeC_2H_5$, 110615-19-5; $(p\text{-}CH_3OC_6H_4Te)_2$, 35684-37-8; $(n\text{-}C_{12}H_{25}Te)_2$, 91913-41-6; $(n\text{-}C_4H_9Te)_2$, 77129-69-2; $(C_2H_5Te)_2$, 26105-63-5; $(PhCH_2CH_2Te)_2$, 110615-20-8; $((CH_3)_2CHTe)_2$, 51112-73-3; $(CH_3CH_2CH_2CH(CH_3)Te)_2$, 110615-21-9; $n\text{-}C_{12}H_{25}MgBr$, 15890-72-9; C_4H_9MgBr, 693-03-8; $(n\text{-}C_{12}H_{25})_2Te$, 110615-22-0; $(n\text{-}C_4H_9)_2Te$, 38788-38-4; $n\text{-}C_4H_9TeCH_2CH_2Ph$, 110615-23-1; $PhCH_2CH_2TeC_{12}H_{25}\text{-}n$, 110615-24-2; $(CH_3)_2CHTeC_{12}H_{25}\text{-}n$, 110615-25-3; $n\text{-}C_{12}H_{25}TeC_4H_9$, 110615-26-4; $(CH_3)_2CHTeC_4H_9$, 83817-25-8; $PhCH = CHTeC_4H_9$, 108162-27-2; $PhCH = CHTeC_{12}H_{25}$, 110615-27-5; $PhCH = CHTeC_2H_5$, 110615-28-6.

---

(23) Basmadjan, G. P.; Parker, G. R.; Magarian, R. A.; Kirschner, A. S.; Ice, R. D.; Stanley, M. L. *Int. J. Appl. Radiat. Isot.* **1980**, *517*, 31.

(24) Burstall, F. H.; Sudgen, S. *J. Chem. Soc.* **1930**, 229.