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Synthesis of (E)-1,4-bis(organyl) but-1-en-3-ynes by Lithium-Tellurium Exchange Reaction on (Z)-1-Butyltelluro-1,4-bis(organyl) but-1-en-3-ynes[1].

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Abstract: *1,4-bis(organyl)-1,3-butadiynes react with dibutyl ditelluride and sodium borohydride in ethanol under reflux to give (Z)-1-butyltelluro-1,4-bis(organyl) but-1-en-3-ynes, which by treatment with butyllithium followed by water give (E)-1,4-bis(organyl) but-1-en-3-ynes in high yields.*

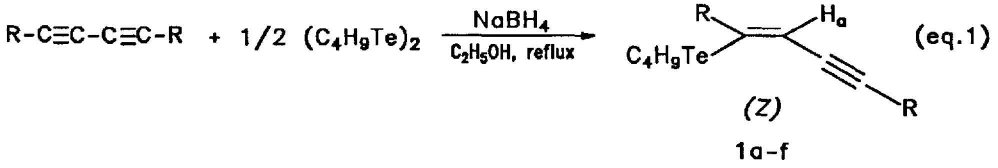
Hydrometallation of acetylenes is a widely used method for the synthesis of vinylic metal and metalloid derivatives. Over the last few years we have reported several methods for the synthesis of vinylic tellurides,[2-5] including the hydrotelluration of terminal acetylenes.[3-5] This type of reaction has also been studied by others.[6-13] We also extended our studies of hydrotelluration to conjugated enynes, obtaining tellurobutadienes by the addition of tellurolate anions to the terminal triple bond.[5]

Vinylic tellurides are an interesting class of organotellurium compounds in organic synthesis.[5,11,13-17] One of the most important reactions of this class, the lithium-tellurium exchange[18], leads to vinyl lithium species of defined configuration.[5,14-16] However, no transmetallation reaction of no-cyclic conjugated tellurium-containing systems have been described thus far.[19]

In this communication we report on the synthesis of (Z)-1-Butyltelluro-1,4-bis(organyl) but-1-en-3-ynes and the study of Li/Te exchange reaction of these conjugated compounds with butyllithium.

Compounds **1a-f** were obtained in good yields[20] by reaction of dibutyl ditelluride (0.5 equiv.) with sodium borohydride in ethanol in the presence of 1,4-bis(organyl)-1,3-butadiynes[21] (eq. 1), refluxing the mixture for the time reported in table 1.

This reaction occurs with 100% of regio- and stereoselectivity. In all cases, only the (Z) product was obtained, as a result of the anti-addition of sodium butyl tellurolate to carbon 1 of the symmetrical butadiyne (eq. 1). The products are stable yellow oils and were identified by IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy. For Compounds **1a-c** the regio- and stereochemistry was easily determined on the basis of multiplicity and coupling constants of ^{1}H NMR vinylic protons signals, in the 5.92-6.36 ppm range. Analogously, the vinylic proton singlet chemical shift for compounds **1d-f** is in the range of 6.29-6.34 ppm (Table 1).



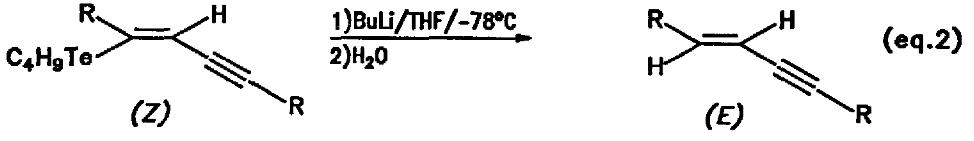
^{13}C-NMR spectra of compounds **1a-f** reveal a signal in the range of 122.2-134.2 ppm due to the tellurium-substituted olefinic carbon and other signal in the range of 114.0-116.2 due to carbon 2. These last signals were assigned by using two dimensional ^{1}H-^{13}C chemical shift correlations.

Table I. Tellurobutenynes prepared.

Compound[a]	R	Proton H_a resonance	^{13}C chemical shifts		Reaction time (h)	Yield(%)[b]
			C_2	C_1		
1a	$-CH_2OH$	6.36 (t,J≈1.3,1H)	114.0	134.2	0.25	71
1b	-H	6.34 (dd,J10.6,J2,1H)	116.2	122.2	0.25	93[c]
1c	$-CH_3$	5.92 (m,1H)	114.1	128.5	2.5	81
1d	$-C_6H_5$	6.34 (s,1H)	116.0	132.3	2.5	89
1e	$4-CH_3C_6H_4-$	6.32 (s,1H)	115.8	131.2	3.0	73
1f	$4-CH_3OC_6H_4-$	6.29 (s, 1H)	115.4	130.7	3.0	68

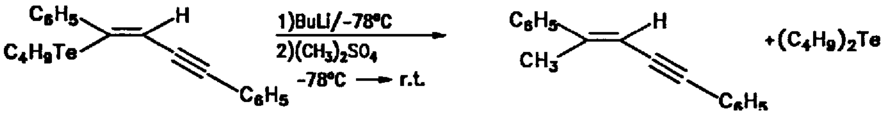
a.Satisfactory elemental analysis were obtained for all compounds synthesized.
b.The products were purified by flash chromatography using hexane or hexane/AcOEt mixture as eluent.
c. Butyl tellurolate was added at room temperature to a large excess of diacetylene.

The reaction of (Z)-1-Butyltelluro-1,4-bis(organyl) but-1-en-3-ynes **1d-f** with 1.1 equivalent of butyllithium in tetrahydrofuran at -78°C followed by water addition produces the corresponding (E)-1,4-bis(organyl) but-1-en-3-ynes as white solids in good yields[22] (eq. 2, table II). This stereochemistry is clearly indicated by coupling constant (J = 16 Hz) of doublets attributed to olefinic protons, characteristic of trans vinyl coupling. The Li/Te exchange reaction of the organotellurium moiety bonded at the sp^2-carbon atom of the conjugated enyne provides an efficient method for obtaining enynyl lithium intermediates of defined configuration, since none configurational inversion at the double bond is observed even when the temperature rises from -78°C to room temperature, before trapping the lithium intermediate. It must be pointed out that halogen/lithium exchange in conjugated systems such as enynyl bromides and butadienyl bromides[23] occurs with a lack of configuration of double bonds.



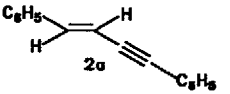
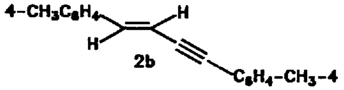
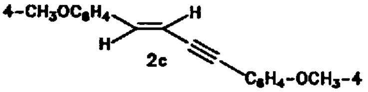
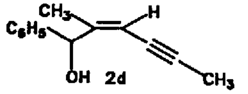
1d-f **2a-c**

The lithium intermediate obtained from the dimethylated compound **1c** reacts with benzaldehyde, yielding the corresponding allylic alcohol **2d** in 63% yield (entry 4, Table II). Similarly, the intermediate 1,4-diphenyl but-3-yne-1-enyl lithium was alkylated in 93% yield with dimethyl sulfate at -78°C for 30 minutes followed by stirring at room temperature overnight (eq. 3).



(eq.3)

Table II. Tellurium free 1,3-butenynes obtained.

Entry	Product[a]	m.p. (°C) or b.p. (°C/mmHg)	Yield(%)
1	 2a	96-97	90
2	 2b	144-146	70
3	 2c	148-149	84
4	 2d	150°C/1mmHg	63

a.Satisfactory elemental analysis were obtained for all compounds synthesized.

The results here reported show that the hydrotelluration of dimmeric acetylenes followed by detelluration of tellurobutenyne intermediates with butyllithium is an efficient method for the synthesis of (E)-1,3-butenynes. Investigations on the selective addition to the triple bond of unsymmetrical diacetylenes and detelluration of the intermediates, to obtain butenynes isolated from natural sources,[24] are now in progress.

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20. 1,3-Butadiynes are potentially available by a wide variety of procedures. For a comprehensive list of references, see: Larock, R.C.; "Comprehensive Organic Transformations" p.304, VHC Publishers, Inc., New York, 1989.

21. **Typical procedure for the preparation of (Z)-1-butyltelluro-1,4-bis(organyl) but-1-en-3-ynes:**

To a solution of 1,6-dihydroxi,hexa-2,4-diyne (0.11g; 1.0 mmol) and dibutyl ditelluride (0.184 g; 0.5 mmol) in 95% ethanol (20 mL) under N_2, sodium borohydride (0.045 g; 1.25 mmol) was added at room temperature. After the red color disappearence, the yellow mixture was refluxed for 15 min., allowed to reach room temperature, diluted with ethyl acetate (40 mL) and washed with brine (20 mL x 3). After drying the organic phase ($MgSO_4$), the solvent was removed under reduced pressure and the residue purified by flash chromatography on silica gel eluting with hexane/ethyl acetate (7/3), to give the butyltelluro enyne **1a**. Yield: 0.21 g (71%); IR.: 1581 cm^{-1}, 2225 cm^{-1}, 3325 cm^{-1}; ^{1}H-NMR (δ in $CDCl_3$): 0.91 (t, J7, 3H); 1.38 (sext., J7, 2H); 1.78 (quint., J7, 2H); 2.9 (t, J7, 2H); 3.31 (broad s, 2H); 4.29 (d, $J\approx2.5$, 2H); 4.43 (d, $J\approx2.5$, 2H); 6.40 (t, $J\approx2.5$, 1H); ^{13}C-NMR (d in $CDCl_3$): 5.2, 13.1, 24.7, 33.6, 50.9, 60.3, 84.6, 93.9, 114.0, 134.2; Elemental analysis: Calcd. for 1a $C_{10}H_{16}TeO_2$: C, 40.59; H, 5.41; Found: C, 40.77; H, 5.48.

22. **Typical procedure for the preparation of (E)-1,4-bis(organyl) but-1-en-3-ynes:**

To a solution of **1d** (0.387 g; 1.0 mmol) in THF (6 mL) at -78°C under N_2, butyllithium (0.67 mL, 1.1 mmol, 1.5 M in hexane) was added at once and the reaction stirred for 15 min. The cooling bath was removed and the mixture treated with saturated solution of ammonium chloride (5 mL), diluted with ethyl acetate (15 mL) and washed with brine (15 mL x 3). After drying the organic phase ($MgSO_4$), the solvent was removed under vacuum and the residue purified by flash chromatography on silica gel using hexane as eluent. Hexane was partially evaporated to give white crystals of the (E)-enyne **2a**. Yield: 0.174 g (85%). Recrystallized from ethanol: m.p. 96-97°C; MS m/e 204 (M^+); ^{1}H-NMR (δ in CCl_4): 6.3 (d, J16, 1H); 6.98 (d, J16, 1H); 7.1-7.5 (m, 10H); ^{13}C-NMR: 89.0, 91.8, 108.1, 141.1, 123.4, 126.2, 128.0, 128.2, 128.5, 128.6, 131.4,136.2. Elemental analysis: Calcd. for $C_{16}H_{12}$: C, 94.08; H, 5.92; Found: C, 93.94; H, 5.89.

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