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VINYLLITHIUMS FROM BUTYL-VINYL TELLURIDES AND BIS-VINYL TELLURIDES

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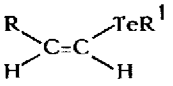
ABSTRACT: Butyl vinyl tellurides and bis-vinyl tellurides furnish vinyllithiums with retention of configuration in good yields upon treatment with n-butyllithium at -78°C.

Vinylic tellurium species are little investigated. Recently we initiated a systematic study of this class of organoelemental compounds and developed several methods for their preparation[1-4]. In this communication we report the use of butyl vinyl tellurides (1) and bis-vinyl tellurides (2) as efficient sources of vinyllithiums.



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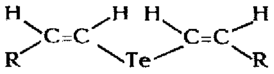


2

This synthetic operation takes advantage of the softness of the tellurium atom[5]. In this way, by treating 1 (R^1 = n-C_4H_9) with 1 equivalent of n-butyllithium at -78°C, followed by trapping the intermediate vinyllithium[6] with electrophiles, the vinylic derivatives (3) were isolated in good yields (Eq. 1, Table 1)[7].

$$\underline{1}\ \xrightarrow[-\text{BuTeR}^1]{n\text{-BuLi,THF,-78°C,N}_2}\ [\text{RCH=CHLi}]\ \xrightarrow[-78°\text{C}]{\text{E}^+\text{, THF}}\ \underset{\underline{3}}{\text{RCH=CHE}} \qquad (1)$$

R^1 = Bu

$E^+ = C_6H_5CHO,\ (C_6H_5)_2CO,\ \overline{CH_2(CH_2)_4CO},\ C_8H_{17}Br$

In all cases shown in Table 1 the configuration of the carbon-carbon double bond of the olefin (3) and that of the starting alkyl vinyl telluride (1) was the same. A complex mixture of products (analysed by GC-MS) was formed when an aryl vinyl telluride (4) was treated with an equivalent amount of n-butyllithium and then trapped with benzaldehyde. Scheme 1 rationalizes this result.

Scheme 1

Path 1: $$\underset{\underline{4}}{ArTeCH{=}CH_2} \xrightarrow{n\text{-BuLi}} \underset{\underline{5}}{CH_2{=}CHLi} + \underset{\underline{6}}{ArLi} + \underset{\underline{7}}{ArTeBu} + \underset{\underline{8}}{BuTeCH{=}CH_2}$$

Path 2: $$\underline{7}, \underline{8} \xrightarrow{n\text{-BuLi}} \underline{5} + \underline{6} + \underset{\underline{9}}{BuTeBu}$$

Path 3: $$\underline{4} + \underline{6} \longrightarrow \underset{\underline{10}}{Ar_2Te} + \underline{5}$$

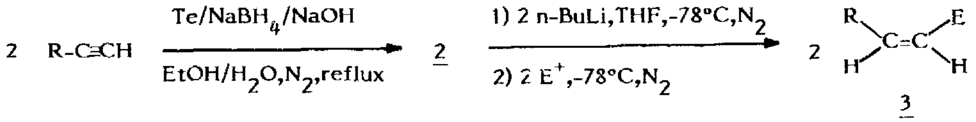
Path 4: $$\underline{5}, \underline{6} \xrightarrow{C_6H_5CHO} \underset{\underline{11}}{CH_2{=}CHCH(OH)C_6H_5} + \underset{\underline{12}}{ArCH(OH)C_6H_5}$$

Ar = C_6H_5; p-$CH_3OC_6H_4$

In path 1 n-butyllithium attacks the tellurium atom of 4 leading to a mixture of vinyllithium (5),aryllithium (6), butyl aryl telluride (7) and butyl vinyl telluride (8); in path 2, n-butyllithium attacks the tellurium atom of 7 or 8 formed in path 1 leading to 5 or 6 and to dibutyl telluride (9); in path 3, 6 attacks the tellurium atom of 4 leading to 5 and diaryl telluride (10), which can react with 5 regenerating 4. Addition of benzaldehyde to the reaction mixture (path 4) leads to a mixture of 11 and 12 in a 55/45 ratio. The propositions shown in paths 2 and 3 were confirmed by using an excess of n-butyllithium. In this case no starting material (4), butyl-aryl telluride (7) or diaryl telluride (10) were detected among the reaction products; only 9, 11 and 12 were detected. The results commented above show that an alkyl group must be attached to the tellurium atom of 1 to avoid the formation of a mixture of products. In this work we used butyl vinyl tellurides obtaining dibutyl telluride as by-product, which was easily separated from the reaction mixture by chromatography on silica gel.

Recently we developed an efficient method to prepare bis-vinyl tellurides (2) of Z configuration by reacting acetylenes with disodium telluride generated in situ from elemental tellurium and sodium borohydride/sodium hydroxide in ethanol-water (Eq.2)[4,8].

Treatment of the bis-vinylic tellurides (2) with 2 equivalents of n-butyllithium in tetrahydrofuran at -78C°, followed by trapping the intermediate vinyllithium with electrophiles gave the corresponding olefines (3) in good yields. In this way, the bis-vinyl tellurides (2) are source of two equivalents of vinyllithiums (Eq.2, Table 1).

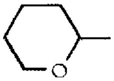


$$2\ \ R\text{-}C{\equiv}CH \xrightarrow[EtOH/H_2O,N_2,reflux]{Te/NaBH_4/NaOH} 2\ \ \underline{2} \xrightarrow[2)\ 2\ E^+,-78°C,N_2]{1)\ 2\ n\text{-BuLi,THF},-78°C,N_2} 2 \qquad (2)$$

$\underline{3}$

$E^+ = C_6H_5CHO,(C_6H_5)_2CO, \overline{CH_2(CH_2)_4C}{=}O, C_8H_{17}Br$

Table I - Reaction of butyl vinyl tellurides (method A) or bis-vinyl tellurides (method B) with n-butyllithium followed by trapping with electrophiles.

Product[a]	Yield (%)[b] A	Yield (%)[b] B	Product[a]	Yield (%)[b] A	Yield (%)[b] B
$Z\text{-}C_6H_5CH{=}CHCH(OH)C_6H_5$	85[d]	80[g]	$(CH_3)_2C{=}CHCH(OH)C_6H_5$	76[e]	—
$Z\text{-}C_6H_5CH{=}CHC(C_6H_5)_2OH$	—	89	$Z\text{-}C_6H_5CH{=}CH\overline{C(OH)(CH_2)_4C}H_2$	79	82
$Z\text{-}C_6H_5CH{=}CH(CH_2)_7CH_3$	70[i]	70[i]	$CH_2{=}CHC(C_6H_5)_2OH$	70	—
$E\text{-}C_6H_5CH{=}CHCH(OH)C_6H_5$	79[c]	–	$CH_2{=}C(CH_3)CH(OH)C_6H_5$	–	72[f]
$CH_2{=}CHCH(OH)C_6H_5$	85[e]	80[f]	$p\text{-}BrC_6H_4CH{=}CHCH(OH)C_6H_5$	–	66[g,h]
$CH_3CH{=}CHCH(OH)C_6H_5$	81[e]	–	$p\text{-}CH_3C_6H_4CH{=}CHCH(OH)C_6H_5$	–	70[g]
$CH_3CH{=}CH(CH_3)CH(OH)C_6H_5$	79[e]	–	 $NCH_2CH{=}CHCH(OH)C_6H_5$	70[d]	73[g]
$CH_2{=}C(C_6H_5)CH(OH)C_6H_5$	77[e]	–	 $OCH_2CH{=}CHCH(OH)C_6H_5$	72[d]	72[g]

[a] All compounds gave satisfactory ^1H NMR, ^{13}C NMR and mass spectral data; [b] yield of the product purified by column chromatography; [c] prepared by vinylic substitution of lithium butyltellurolate on commercial trans-β-bromostyrene[1], contaminated with 10% of the cis isomer. This percentage of cis isomer was observed both in vinylic tellurides and in the allylic alcohol; [d] the starting vinylic telluride was prepared by reaction of the corresponding acetylenic telluride with sodium borohydride in ethanol under reflux[3]; [e] the starting butyl vinyl telluride was prepared by reaction of the vinyl Grignard reagents with tellurium followed by alkylation with butyl bromide. [f] the starting bis vinylic telluride was prepared by reacting vinyltellurenyl bromides ($CH_2{=}CRTeBr$, obtained by brominolisis of the corresponding divinylditellurides[3]) with Grignard reagents; [g] the starting bis vinylic telluride was prepared by reacting acetylenes with disodium telluride in ethanol under reflux[4]; [h] in this case a 92:8 mixture of Z/E allylic alcohols was detected by 200 MHz ^1H NMR and CG-MS; [i] after the addition of the 1-bromooctane dissolved in THF (5 ml) the reaction mixture was stirred at room temperature for 12 h.

As in the case of the butyl vinyl tellurides the transmetallation reaction occurred with retention of configuration.

The results reported in this communication show that alkyl vinyl tellurides (1) and bis-vinylic tellurides (2) are valuable intermediates in organic synthesis. New methods of synthesis and new synthetic uses for these compounds are presently under investigation in our laboratory.

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6. Two isolated examples of this reaction were reported in the literature: [a]T. Kauffmann and H. Allers, Chem. Ber., 116, 1001 (1983); [b]T. Hiiro, N. Kambe, A. Ogawa, N. Miyoshi, S. Muray and N. Sonoda, Angew. Chem. Int. Ed. Engl. 26, 1187 (1987).
7. Typical procedure: To a solution of the butyl vinyl telluride (1 mmol) in THF (4 ml) at -78°C under nitrogen was added dropwise a solution of n-BuLi (0.67 ml, 1 mmol, 1.5 M solution in hexane). After 40 min of stirring at this temperature, benzaldehyde (106 mg, 1 mmol) was added. The reaction mixture was allowed to reach room temperature (30 min), then was diluted with ethyl acetate (40 ml), and washed with brine (4x15 ml). The organic layer was worked up in the usual way and the residue was purified by column chromatography on silica gel. Elution with hexane removed dibutyltelluride and elution with ethylacetate the product. The reaction of bis-vinylic tellurides with n-butyllithium followed by capture with benzaldehyde was performed using the same procedure described above; two equivalents of n-butyllithium and two equivalents of benzaldehyde were used per equivalent of bis-vinylic telluride.
8. An isolated example of this class of compounds [Z-$(C_6H_5CH{=}CH)_2Te$] was recently prepared in 15% yield by reacting phenyl acetylene with tellurium in aqueous medium in the presence of a reducing agent: V.A. Potapov, S.V. Amosova, A.S. Kashik, Tetrahedron Lett., 30, 613 (1989).
   The same compound of E configuration was obtained in 41% yield by vinylic substitution of Na_2Te on trans-β-bromo styrene[1]. K. Ohe, H. Takahashi, S. Uemura, N. Sugita, J.Chem.Soc. Japan, 1469 (1987).

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