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Stereoselective Synthesis of (Z)- or (E)-β-Bromovinyl Tellurides and Their Application in the Synthesis of Trisubstituted Alkenes

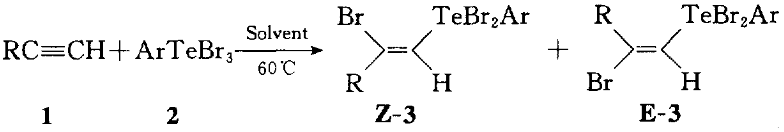
Xian Huang* and Ya-Pin Wang

Department of Chemistry, Hangzhou University, Hangzhou, 310028, P. R. China.

Abstract: Reaction of aryltellurium tribromides with alkynes in methanol affords (E)-β-bromovinyl aryltellurium dibromides and in benzene gives the (Z)-isomer, which can be reduced by sodium borohydride to yield (Z) or (E)-β-bromovinyl tellurides respectively. Copyright © 1996 Elsevier Science Ltd

Recently the applications of tellurium compounds in organic synthesis have been paid more attention.[1-2] Vinyl tellurides have been utilized as important intermediates in the stereoselective formation of olefin derivatives.[3-5] Considering that vinyl bromides can undergo many coupling reactions under the catalysis of transition metal complexes,[6,7] we think that β-bromosubstituted vinyl tellurides are versatile synthetic intermidiates since they have the structural units of both vinyl bromide and vinyl telluride. β-Bromovinyl selenides can be prepared by the reaction of arylselenenyl bromides with alkynes,[8] but this reaction was not suitable to synthesize β-bromovinyl tellurides for the poor stability of aryltellurenyl bromides.

It was reported that aryltellurium tribromides are more stable and can undergo addition reactions with alkenes.[9] We studied the reactivity of aryltellurium tribromides toward alkynes. The experimental results showed that alkynes (**1**) reacted with aryltellurium tribromides (**2**) in methanol or benzene at 60℃ to give β-bromovinyl aryltellurium dibromides (**3**) in good yields.



The reaction is highly regioselective, but the stereoselectivity is related to polarity of the solvent employed. In methanol, a polar solvent in which tellurium ion intermediates might be formed, anti addition products (**E-3**) were obtained almost exclusively. However in benzene, a nonpolar solvent, probably through a four-membered cyclic transition state,[10] Z-isomers (**Z-3**) were obtained by 93—98%. The experimental results are summerized in **Table 1**.

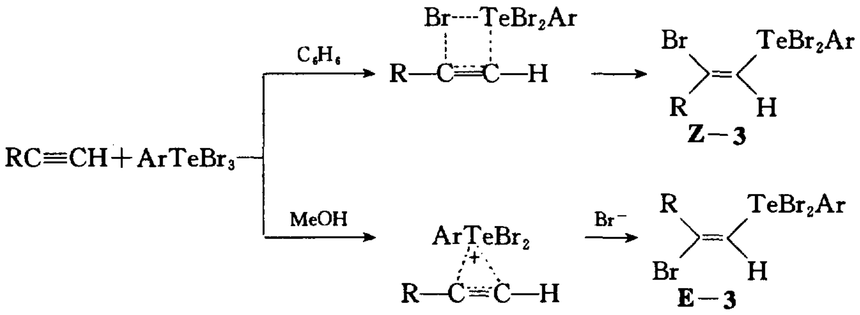


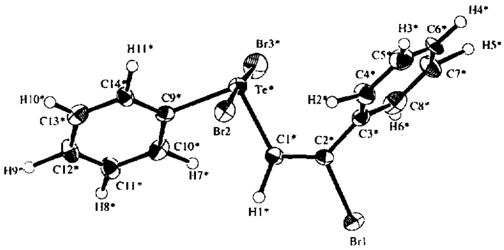
Table 1 Stereoselective Synthesis of (E)-or (Z)-Compounds **3**

Product	R	Ar	Solvent	Yield[a]	E : Z[b]
E-3a	Ph	Ph	MeOH	84	99 : 1
E-3b	CH_3OCH_2	Ph	MeOH	72	99 : 1
E-3c	Ph	4-$CH_3C_6H_4$	MeOH	75	99 : 1
E-3d	CH_3OCH_2	4-$CH_3C_6H_4$	MeOH	68	98 : 2
E-3e	Ph	α-$C_{10}H_7$	MeOH	80	99 : 1
Z-3a	Ph	Ph	C_6H_6	80	5 : 95
Z-3b	CH_3OCH_2	Ph	C_6H_6	70	6 : 94
Z-3c	Ph	4-$CH_3C_6H_4$	C_6H_6	71	7 : 93
Z-3d	CH_3OCH_2	4-$CH_3C_6H_4$	C_6H_6	69	5 : 95
Z-3e	Ph	α-$C_{10}H_7$	C_6H_6	85	2 : 98

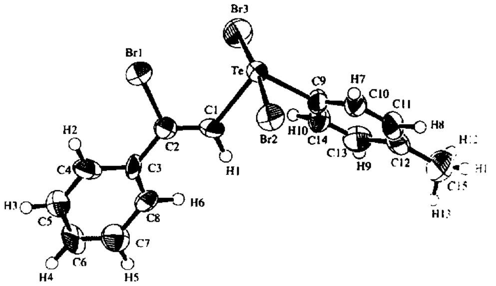
a. Isolated yield. b. Isomer ratio obtained by ^1H NMR.

The structure assignments of products were based on MS, ^1H NMR and NOE experiments. Furthermore the X-ray diffraction results (**fig. 1**) and (**fig. 2**) confirmed the assigned configurations of products.

The bromine complexed with dialkyl sulfides or with trialkylphosphines can be debrominated by many reducing agents.[11] Our experiment results showed that (Z)-or (E)-β-bromovinyl aryltellurium dibromides (1mmol) in THF (15ml) are smoothly reduced by a solution of sodium borohydride (1mmol) in 80% EtOH (15ml) at -5℃ for 10-15 minutes, to give (Z) or (E)-β-bromovinyl aryltellurides (**Z-4**) or (**E-4**) in good yields (**Table 2**).



(fig. 1) E-3a

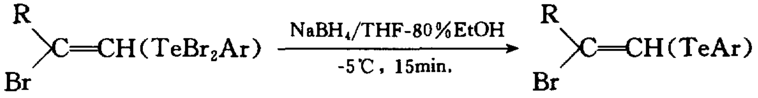


(fig. 2) Z-3c

Table 2 Stereoselective Synthesis of (E)-or (Z)-Compounds **4**

Product^a		R	Ar	Yield^b(%)
E-4a	oil	Ph	Ph	88
E-4b	oil	CH_3OCH_2	Ph	82
E-4c	oil	Ph	$4\text{-}CH_3C_6H_4$	80
Z-4a	oil	Ph	Ph	85
Z-4b	oil	CH_3OCH_2	Ph	80
Z-4c	oil	Ph	$4\text{-}CH_3C_6H_4$	86

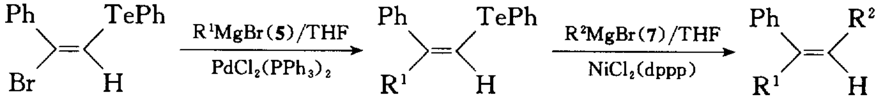
a. Compounds characterized by MS, HRMS, ^{1}HNMR and IR. b. Isolated yield.



$$\text{R(Br)C=CH(TeBr}_2\text{Ar)} \xrightarrow[-5^\circ C,\ 15\text{min.}]{NaBH_4/THF\text{-}80\%EtOH} \text{R(Br)C=CH(TeAr)}$$

Z or E-3 **Z or E-4**

(Z) or (E)-β-Bromovinyl aryltellurides (**4**) are biheteroatom compounds. Because the leaving ability of bromo-group in β-bromovinyl aryltellurides (**4**) was much higher than that of telluro-group, we attempted to develop a new method for the stereoselective synthesis of trisubstituted alkenes by two sequential coupling reactions of β-bromovinyl aryltellurides (**4**). Fox example, in the catalysis of $PdCl_2(PPh_3)_2$(2% mmol), (**E-3a**) (2mmol) reacted with R^1MgBr(**5**) (6mmol) in THF (10ml) at 25°C for 6 hr to give disubstituted vinyltellurides (**6**). Then (**6**) (1mmol) reacted with R^2MgBr(**7**) (3mmol) in presence of $NiCl_2$(dppp) (2% mmol) in THF (5ml) at 25°C for 2-5 hr to give trisubstituted alkenes, with no change of the original configuration.[12]

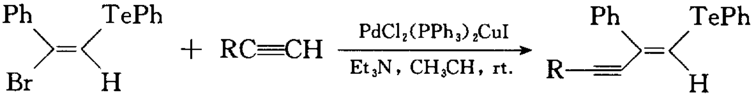


E-4a **6** **8**

R^1= i-Pr, Ph, 4-$CH_3C_6H_4$
Yield of **6**: 79%, 80%, 68%

R^1= i-Pr, Ph, 4-$CH_3C_6H_4$
R^2= Ph, 4-$CH_3C_6H_4$, Et
Yield of **8**: 68%, 66%, 70%

(E)-β-Bromovinyl telluride **E-4a** (1mmol) also reacts with terminal alkynes **9** (1. 2mmol) in the presence of $PdCl_2(PPh_3)_2$-CuI (0. 02mmol) in CH_3CN (5ml), using triethylamine (1mmol) as a base. Stiring overnight at room temperature leads to the stereoselective synthesis of 1,3-enynyl tellurides **10**.



E-4a **9** **10**

R=Ph, $HOCH_2$, CH_3OCH_2, CH_3OOC, n-C_5H_{11}
Yield of **10**: 58%, 62%, 68%, 70%, 68%

Therefore, β-bromovinyl tellurides were promising synthetic intermediates, which could be used in the synthesis of olefines, conjugated enyne and some classes of natural products.

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REFERENCES AND NOTES

1. Mo, X. S. and Huang, Y. Z.; *Tetrahedron Lett.*, **1995**, 35, 3539.
2. Ohe, K.; Takahashi, H.; Uemura, S.; Sugita, N.; *J. Org. Chem.*, **1987**, 52, 4859.
3. Chieffi, A.; Comasseto, J. V.; *Tetrahedron Lett.*, **1994**, 4063.
4. Ogawa, A.; Tsuboi, Y.; Obagashi, R; Yokoyama, K.; Ryu, I. and Sonada, N.; *J. Org. Chem.* **1994**, 59, 1600.
5. Petragnani, N.; Comasseto, J. V.; *Synthesis*, **1991**, 793; **1991**, 897.
6. Kim, J. I.; Patel, B. A.; Heck, R. F.; *J. Org. Chem.*, **1981**, 46, 1067.
7. Murahashi, S. I.; Yamamura, M.; Yanagisawa, K.; Mita, N.; Kondo, K.; *J. Org. Chem.* **1979**, 44, 2408.
8. Chierici, L.; Fernanodo, M.; *Gazz Chim. Ital.*, **1956**, 86, 1296.
9. Uemura, S.; Fukuzawa, S. I.; Toshimitsu, A.; Okano, M.; *Tetrahedron Lett.* **1982**, 23, 1177.
10. Comasseto, J. V.; Stefani, H. A.; Chieffi, A.; *Organometallics*, **1991**, 10, 845.
11. Teffery, W. K.; Slayton, A.; Evans, Jr.; *J. Org. Chem.*, **1986**, 51, 5490.
12. (a) Fiandanese, V.; Marchese, G.; Naso, F.; Ronzini, L.; *Synthesis*, **1987**, 1034.
    (b) Uemura, S.; Fakuzawa, S. I.; *Tetrahedron Lett.*, **1982**, 23, 1181.

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