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ALKYLVINYL TELLURIDES FROM TELLURIUM, ACETYLENE AND ALKYL HALIDES

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Abstract - Synthetic routes to alkylvinyl tellurides by direct reaction of metallic tellurium, acetylene and alkyl halide in the system KOH-$SnCl_2$-H_2O and successive interaction of divinyl telluride with lithium and alkyl halide in liquid ammonia have been developed.

The data available on the preparation and properties of vinylorganotellurides are scarce and related mainly to compounds of the aromatic series. Among the known methods for the synthesis of arylvinyl tellurides the following processes can be mentioned: addition of arenetellurolate anions to substituted activated acetylenes,[1] reduction of bis(2,2-diarylvinyl)tellurium dichlorides,[2] reaction of divinyl mercury with diaryl ditellurides,[3] reaction of vinylmagnesium halides with aryltellurenyl halides.[4] For the first time alkylvinyl tellurides were prepared by us from metallic tellurium, acetylene and alkyl halides which was reported in short communications to claim priority.[5] Recently the synthesis of butylvinyl telluride (yield 64-82%) by alkylation of divinyl ditelluride under phase transfer conditions as well as by reaction of vinylmagnesium bromide with butyltellurenyl halide or successively with metallic tellurium and butyl bromide has been described.[6]

In the present communication the data obtained by us in developing convenient and effective synthetic routes to alkylvinyl tellurides by direct reaction of metallic tellurium, acetylene and alkyl halide and by successive interaction of divinyl telluride with lithium and alkyl halide in liquid ammonia are summarized and discussed.

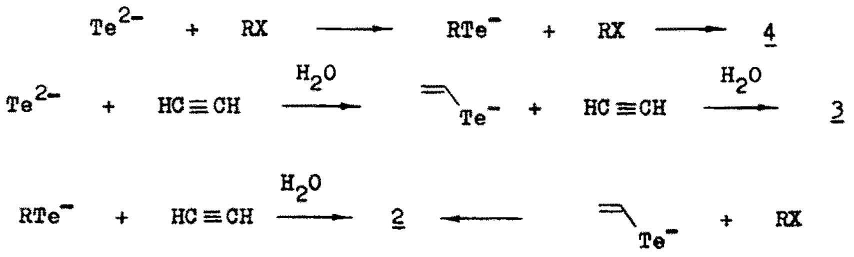
The reaction of tellurium with acetylene and alkyl halides 1 proceeds at 105-115° in a strongly basic reducing system KOH-$SnCl_2$-H_2O. Along with alkylvinyl tellurides 2 divinyl telluride 3 and the corresponding dialkyl tellurides 4 are also formed.

(1)

1a-f 2a-e 3 4a-e

R = Me (a), Et (b), n-Pr (c), i-Pr (d), n-Bu (e), t-Bu (f); X = Cl, Br, I

The processes of alkylation-vinylation, alkylation and vinylation proceed apparently as presented on the next scheme including the reaction of Te^{2-} with alkyl halide and (or) acetylene.



Telluride ions are generated in the reaction mixture under the action of the alkaline reducing system KOH-$SnCl_2$ which probably provokes the following transformations.

$$3\ Te + 6\ KOH \rightleftharpoons 2\ K_2Te + K_2TeO_3 + 3\ H_2O \qquad (2)$$

$$SnCl_2 + 4\ KOH \longrightarrow K_2SnO_2 + 2\ KCl + 2\ H_2O \qquad (3)$$

$$2\ K_2SnO_2 + K_2TeO_3 + H_2O \longrightarrow Te + 2\ K_2SnO_3 + 2\ KOH \qquad (4)$$

The reactions (2)-(4) can be expressed by the total equation (5):

$$Te + 6\ KOH + SnCl_2 \longrightarrow K_2Te + 2\ KCl + K_2SnO_3 + 3\ H_2O \qquad (5)$$

It should be emphasized that in an aqueous alkali medium reaction (1) does not occur.

Under identical conditions the yield and ratio of the reaction products are significantly dependent on the starting alkyl halides. The applicability of the latter ones in this process drops in the following order of the halogen atom (X) changing: Br > I > Cl (Table 1, runs 1-3). From Table 1 (runs 1, 4-6) it also follows that primary and secondary alkyl bromides are comparatively readily involved in reaction (1). We failed to obtain tert-butylvinyl and di-tert-butyl tellurides (Table 1, run 7), evidently because the tertiary alkyl halides are highly prone to alkaline elimination of hydrogen halides.

The considerable decrease in the product yield in reaction (1) when butyl iodide is used instead of butyl bromide (Table 1, runs 1, 2) may be explained by the fact that the latter reacts with the tellurides 2e, 3, 4e formed, thus leading to the corresponding triorganyltelluronium salts. As known,[7] aliphatic tellurides and alkyl iodides are especially easy to enter the ternization reaction, among which dimethyl telluride and methyl iodide are most reactive, respectively. Furthermore, we have specially demonstrated divinyl telluride* to react easily with alkyl iodides forming earlier unknown alkylvinyl telluronium iodides 5.

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* First synthesized by us from tellurium and acetylene.[8]

 (6)

5a-d

R = Me (a), Et (b), n-Pr (c), n-Bu (d)

Reaction (6) with methyl iodide proceeds quantitatively at room temperature coming to the end within an hour. This makes it quite clear why the previous attempt to obtain methylvinyl telluride by heating methyl iodide, tellurium and acetylene in the system KOH-$SnCl_2$-H_2O turned out unsuccessful (Table 1, run 8). In this case tellurides 3 and 4a were not observed in the reaction mixture.

At the same time, it was possible to suppress to a considerable extent the side reaction of iodomethylation of tellurides 2-4 by decreasing ten-fold the concentration of starting MeI and introducing HMPA thus homogenizing and diluting the reaction mixture. Under these conditions (Table 1, run 9) the yield of methylvinyl telluride, tellurides 3 and 4a amounted to 20, 55 and 8%, respectively.

The yield of alkylvinyl tellurides was substantially increased by using the molar ratio of Te-RX = 10:1, other conditions being equal (0.1 mole Te, 0.87

Table 1

The influence of the structure of alkyl halide on the yield of tellurides 2-4[a]

Run No	RX	Yield, %[b]		
		CH_2=CHTeR (2)	3	R_2Te (4)
1	n-BuBr	38	32	12
2	n-BuI	15	24	7
3	n-BuCl	5	12	–
4	EtBr	35	26	10
5	n-PrBr	36	28	11
6	i-PrBr	33	32	12
7	t-BuBr	–	50	–
8	MeI	–	–	–
9[c]	MeI	20	55	8

[a] Conditions of reaction (1): Te-RX-KOH-$SnCl_2$ = 0.1:0.1:0.87:0.13 (molar), respectively; 150 ml H_2O; 105-115°, 5 hr; acetylene pressure, initial 14-15 atm, residual 7-8 atm; amount of acetylene absorbed 0.8-0.9 mole.

[b] Yield of divinyl telluride is based on tellurium, yields of tellurides 2 and 4 are based on alkyl halides.

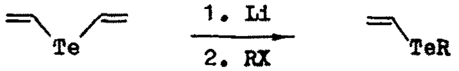
[c] With 80 ml HMPA and 0.01 mole of MeI.

mole KOH, 0.13 mole $SnCl_2$, 150 ml H_2O, 105-115°, 5 hr, initial acetylene pressure 13-15 atm, residual pressure 7-8 atm, acetylene absorbed 0.8-0.9 mole).

Alkyl halide RX	Yield of CH_2=CHTeR, % 0.1 mole RX	0.01 mole RX
EtBr	35	69
n-PrBr	36	68
i-PrBr	33	65
n-BuBr	38	70

In these runs the yield of divinyl telluride ranged 53-60%, the yield of the corresponding dialkyl tellurides is 4-7%.

Alkylvinyl tellurides were also successfully synthesized by consecutive interaction of divinyl telluride with lithium and alkyl halide in liquid ammonia.



(7)

2a-c

RX = MeI, EtBr, n-PrBr

The yield of vinyl tellurides 2 is 30% when methyl iodide is used and about 60% with alkyl bromides.

The spectral parameters of alkylvinyl tellurides are presented in Table 2.

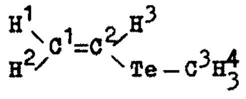
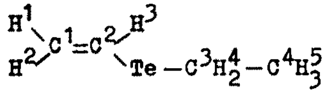
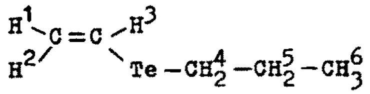
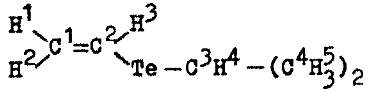
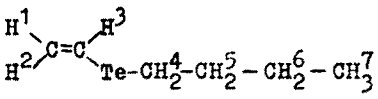
EXPERIMENTAL

^{13}C NMR spectra were run on a Bruker WP-200SY spectrometer, ^{1}H NMR spectra on a Tesla BS-487C spectrometer (80 Hz). IR spectra were recorded on a Specord 75 IR instrument, UV spectra on a double-beam Specord UV VIS spectrophotometer. Mass spectra were obtained on a MAT-212 spectrometer. The reaction mixture was analysed by GLC (chromatograph LHM-8M, column: 100 x 3 mm with 15% Carbowax 6000 on Chromaton N-AW-DMCS). Individual alkylvinyl tellurides synthesized by scheme (1) were isolated by preparative GLC (chromatograph PAHV-07, column: 1200 x 10 mm packed as analytical one).

Methylvinyl telluride (2a) (Scheme 1). 12.8 g Te, 1.42 g of methyl iodide, 48.7 g KOH, 24.7 g $SnCl_2$, 80 ml HMPA and 70 ml H_2O were heated (105-115°) in a rotating autoclave 1 l under acetylenic pressure (initial pressure 14 atm, residual pressure 7 atm, absorbed acetylene 0.8 mole) for 5 hr. The reaction mixture is evacuated at 1 mm Hg. The fraction (10.5 g) collected into a cooled trap (-70°) contains, according to GLC data, methylvinyl telluride 0.34 g (yield 20%), divinyl telluride 10 g (yield 55%) and dimethyl telluride 0.12 g (yield 8%). For 2a: b.p.$_{720}$ 115-116°, n_D^{20} 1.6182. (Found: C, 21.48; H, 3.49; Te, 75.35. Calc. for C_3H_6Te: C, 21.24; H, 3.56; Te, 75.20%). $M^{+\cdot}$ 172.

Ethylvinyl telluride (2b) (Scheme 1). 2.8 g Te, 1.1 g of ethyl bromide, 48.7 g KOH, 24.7 g $SnCl_2$ and 150 ml H_2O are heated (105-115°) in a rotating autoclave 1 l under acetylenic pressure (initial pressure 15 atm, residual pressure 8 atm, amount of absorbed acetylene 0.9 mole) for 5 hr. The lower organic layer is removed from the reaction mixture, dried with KOH and fractionated at 1 mm Hg. The

Table 2. Spectral parameters of alkylvinyl tellurides (<u>2a-e</u>)

	Compound	NMR, ppm (^{1}H in CCl$_4$; ^{13}C in CD$_3$COCD$_3$; J, Hz)	IR spectra, cm^{-1}	UV spectra, λ_{max}, nm (ε) in heptane
2a		7.02 dd (H^3), 6.10 d (H^1), 5.56 d (H^2), 1.96 c (H^4); 124.92 (C^1), 107.92 (C^2), 21.02 (C^3); $J_{H^2H^3}$ 17.8, $J_{H^1H^3}$ 10.6	3061, 3004 ν(=CH$_2$, =CH), 2982, 2921 ν(C-H), 1574 ν(C=C), sh 1422, 1414 δ(CH$_3$), 1375 δ(CH$_2$), 1240, 1214 δ (=CH$_2$, =CH), 987, 964 τ(CH$_2$), 892, 834 ω(=CH$_2$), 519 ν(C-Te)	232 (4920), sh 249 (3780), 266 (4820), 331 (315), sh 380 (60)
2b		7.04 dd (H^3), 6.26 d (H^1), 5.76 d (H^2), 2.96 q (H^4), 1.67 t (H^5); 126.78 (C^1), 107.86 (C^2), 17.79 (C^3), 1.92 (C^4); $J_{H^2H^3}$ 17.5, $J_{H^1H^3}$ 10.2	3060, 3010 ν(=CH$_2$, =CH), 2980, 2950, 2920, 2860 ν(C-H), 1572 ν(C=C), 1440 δ(CH$_3$), 1370 δ(=CH$_2$), 1230, 1185 δ(=CH$_2$, =CH), 960 τ(=CH$_2$), 515 ν (C-Te)	230 (4570), sh 251 (2905), 267 (4190), 332 (450), sh 382 (70)
2c		6.96 dd (H^3), 6.15 d (H^1), 5.68 d (H^2), 2.64 t (H^4), 1.78 m (H^5), 0.96 t (H^6); $J_{H^2H^3}$ 17.6, $J_{H^1H^3}$ 10.3	3060, 3010 ν(=CH$_2$, =CH), 2985, 2960, 2925, 2890, 2870, 2850 ν(C-H), 1570 ν(C=C), 1450 δ(CH$_3$), 1370 δ(=CH$_2$), 1270, 1235, 1175, 1165 δ(=CH$_2$, =CH), 960 τ(=CH$_2$), 840 ω(=CH$_2$), 515 ν(C-Te)	229 (4525), sh 250 (2895), 268 (4630), 329 (380), sh 385 (70)
2d		7.08 dd (H^3), 6.35 d (H^1), 5.84 d (H^2), 3.40 m (H^4), 1.64 d (H^5); 128.93 (C^1), 107.87 (C^2), 26.86 (C^3), 13.30 (C^4); $J_{H^2H^3}$ 17.5, $J_{H^1H^3}$ 10.2	3060, 3010 ν(=CH$_2$, =CH), 2965, 2940, 2915, 2855 ν(C-H), 1575 ν(C=C), 1460, 1378 δ(CH$_3$), 1365 δ(=CH$_2$), 1235, 1195, 1145 δ(=CH$_2$, =CH), 965 τ(=CH$_2$), 900 ω(=CH$_2$), 520 ν(C-Te)	229 (5325), sh 252 (2685), 268 (3520), 333 (410), sh 386 (70)
2e		7.01 dd (H^3), 6.21 d (H^1), 5.74 d (H^2), 2.70 t (H^4), 1.75 m (H^5), 1.38 m (H^6), 0.94 t (H^7); $J_{H^2H^3}$ 17.5, $J_{H^1H^3}$ 10.2	3060, 3010 ν(=CH$_2$, =CH), 2980, 2950, 2925, 2865, 2855 ν(C-H), 1573 ν(C=C), 1460 δ(CH$_3$), 1370 δ(=CH$_2$), 1230, 1180, 1160 δ(=CH$_2$, =CH), 960 τ(=CH$_2$), 885 ω(=CH$_2$), 510 ν(C-Te)	228 (3890), sh 251 (2710), 267 (4165), 328 (360), sh 379 (60)

fraction (11.5 g) collected into a cooled (-70°) trap contains, according to GLC data, ethylvinyl telluride 1.27 g (yield 69%), divinyl telluride 10 g (yield 55%), diethyl telluride 0.11 g (yield 6%). For 2b: b.p.$_{720}$ 138°, n_D^{20} 1.5865. (Found: C, 26.35; H, 4.55; Te, 69.76. Calc. for C_4H_8Te: C, 26.15; H, 4.39; Te, 69.46%).

Alkylvinyl tellurides (2c-e) were obtained from tellurium, acetylene and corresponding alkyl bromide in an analogous way. For 2c: yield 68%, b.p.$_{10}$ 60-62°, n_D^{20} 1.5614. (Found: C, 30.55; H, 5.14; Te, 64.25. Calc. for $C_5H_{10}Te$: C, 30.38; H, 5.09; Te, 64.54%). For 2d: yield 65%, b.p.$_{17}$ 71-73, n_D^{20} 1.5622. (Found: C, 30.60; H, 5.24; Te, 64.90. Calc. for $C_5H_{10}Te$: C, 30.38; H, 5.09; Te, 64.54%). For 2e: yield 70%, b.p.$_3$ 52-54° (lit.,[6] b.p.$_4$ 60°), n_D^{20} 1.5503. (Found: C, 34.30; H, 5.90; Te, 60.40. Calc. for $C_6H_{12}Te$: C, 34.03; H, 5.70; Te, 60.27%). $M^{+\cdot}$ 214.

Propylvinyl telluride (2c) (Scheme 7). To a mixture of 1.8 g of divinyl telluride and 200 ml of liquid ammonia 0.14 g of metallic lithium in small pieces (portions) upon stirring (until complete dissolution) and 1.5 g of propyl bromide are added slowly. The ammonia is evaporated and the precipitate is dissolved in water, extracted with ether, dried with K_2CO_3 and fractionated giving 1.25 g (yield 63%) of vinyl telluride 2c.

The synthesis of vinyl tellurides 2a,b is performed in a similar manner with 30 and 57% yield, respectively.

Methyldivinyl telluronium iodide (5a) (Scheme 6). To a solution of 5.1 g divinyl telluride in 8 ml of ethanol 4.5 g of methyl iodide is added dropwise at room temperature, the reaction mixture is being stirred for 4 hr. The precipitate is filtered off, washed with ether, dried in vacuum, thus 8.5 g (yield 93%) of iodide 5a being obtained, m.p. 117° (dec.). (Found: C, 18.56; H, 2.80; I 39.23; Te, 39.43. Calc. for C_5H_9ITe: C, 18.50; H, 2.71; I, 39.37; Te, 39.56%).

Alkyldivinyl telluronium iodides (5b-d) were synthesized in analogous way from divinyl telluride and ethyl iodide, propyl iodide or butyl iodide, respectively, in ethanol at room temperature for 3 hr (5b) and for 6 days (5c,d). For 5b: yield 65%, m.p. 119° (dec.). (Found: C, 21.34; H, 3.28; I, 37.59; Te, 37.80. Calc. for $C_6H_{11}ITe$: C, 21.35; H, 3.29; I, 37.40; Te, 37.99%). For 5c: yield 60%, m.p. 98° (dec.). (Found: C, 24.12; H, 3.90; I, 36.40; Te, 36.00. Calc. for $C_7H_{13}ITe$: C, 23.91; H, 3.72; I, 36.09; Te, 36.20%). For 5d: yield 55%, m.p. 115° (dec.). (Found: C, 26.30; H, 4.15; I, 34.80; Te, 35.00. Calc. for $C_8H_{15}ITe$: C, 26.27; H, 4.13; I, 34.71; Te, 34.89%).

REFERENCES

1. S.P.Buzilova, I.D.Sadekov, T.V.Lipovich et al., *Zh. Obshch. Khim.* 47, 1999, (1977); S.Uemura, S.Fukuzawa, *Tetrahedron Lett.* 23, 1181 (1982); S.Uemura, S. Fukuzawa, S.R.Partil, *J. Organometal. Chem.* 243, 9 (1983); M.R.Detty, B.J. Murray, D.L.Smith, N. Zumbulyadis, *J. Am. Chem. Soc.* 105, 875 (1983); M.R. Detty, B.J.Murray, *J. Am. Chem. Soc.* 105, 883 (1983).
2. D.Elmaleh, S.Patai, Z.Rappoport, *J. Chem Soc.* 3100 (1971); L.Engman, *Organometallics* 3, 1308 (1984); M.Albeck, S.Shaik, *J. Chem. Soc. Perkin Trans I* 1223 (1975); M.de Moura Campos, N.Petragnani, *Tetrahedron* 18, 527 (1962).
3. T.I.Bichkova, G.A.Kalabin, D.F.Kushnarev, *Zh. Org. Khim.* 17, 1329 (1981).
4. T.Kaufman, *Angew. Chem.* 94, 413 (1982).
5. B.A.Trofimov, N.K.Gusarova, A.A.Tatarinova et al., *Zh. Org. Khim.* 20, 1802, (1984); B.A.Trofimov, N.K.Gusarova, A.A.Tatarinova et al., *USSR Pat.* 1203088. Priority 15.05.1984. *Bull. Izobr.* No 1 (1986); B.A.Trofimov, V.A.Potapov, N.K.Gusarova et al., *Zh. Org. Khim.* 21, 1130 (1985).
6. M.J.Dabdoub, V.B.Dabdoub, J.V.Comasseto, N.Petragnani, *J. Organometal. Chem.* 308, 211 (1986).
7. I.D.Sadekov, A.A.Maksimenko, V.I.Minkin, *The Chemistry of Tellurium Organic Compounds*, Rostov-na-Donu Univ. Press., Rostov-na-Donu, 1983.
8. B.A.Trofimov, N.K.Gusarova, S.V.Amosova, *Zh. Org. Khim.* 13, 456 (1977); B.A. Trofimov, S.V.Amosova, N.K.Gusarova, G.K.Musorin, *Tetrahedron* 38, 713 (1982). B.A.Trofimov, N.K.Gusarova, A.A.Tatarinova et al., *USSR Pat.* 996411. Priority 05.06.1981. *Bull. Izobr.* No 6 (1983).