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Addition of Organotellurium Trihalides to Acetylenes

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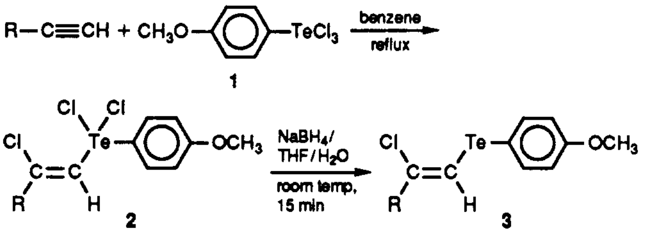
Summary: (*p*-Methoxyphenyl)tellurium trichloride reacts with terminal acetylenes to give 1-chloro-1-organyl-2-[dichloro(*p*-methoxyphenyl)telluro]ethenes of *Z* configuration in good yields. The *Z* stereochemistry of the addition products suggests that the reaction occurs through a four-centered cyclic transition state. The diorganotellurium dichlorides are reduced to the corresponding tellurides with sodium borohydride.

The reaction of aryltellurium halides, leading to vinylic tellurides, has not previously been described. In view of our interest in the chemistry of vinylic tellurides,[1-4] as well as the recent findings concerning the synthetic applications of this class of organotellurium compounds,[5-13] we decided to investigate the addition of aryltellurium trichlorides to acetylenes as a new route to vinylic tellurium species. We found that the reaction of (*p*-methoxyphenyl)tellurium trichloride 1 with 1-alkynes in boiling benzene leads to the vinylaryltellurium dichlorides 2 in good yields (eq 1, Table I) and with high stereoselectivity and regioselectivity.

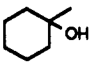


(1)

The vinylic species 2 are stable, colorless, crystalline solids, which can be easily reduced in good yields to the corresponding tellurides 3 by reaction with sodium borohydride in tetrahydrofuran/water at room temperature. The tellurides 3 were isolated as stable yellow oils after column chromatography on silica gel, with hexane as eluent.

Table I

R-C≡CH + $CH_3OC_6H_4TeCl_3$ → 2 → 3

	R	reacn time, h	yield, %	
			2[a,c]	3[b,d]
a	C_6H_5	6.0	77	83
b	*p*-CH_3C_6H	4.0	80	87
c	*p*-$CH_3OC_6H_4$	4.0	85	
d	*p*-$C_2H_5OC_6H_4$	2.0	82	
e	*p*-ClC_6H_4	9.0	74	
f	*p*-BrC_6H_4	24.0	78	89
g	CH_2OH	7.0	60	91
h		3.0	60	85
i	C_6H_{11}	4.0	73	90

[a] Yield of recrystallized ($CHCl_3$/petroleum ether) products. [b] Yield of chromatographed products. [c] Typical experiment: (*p*-methoxyphenyl)tellurium trichloride (1.7 g, 5 mmol) was added to phenylacetylene (0.52 g, 5 mmol) in benzene (50 mL). The mixture was refluxed for 6 h, and the reaction was monitored by TLC (eluting with chloroform). After this time the mixture was washed with methanol/water (1:1; 3 × 30 mL) and the organic phase was extracted with chloroform (30 mL). The organic phase was dried with magnesium sulfate, and the solvent was evaporated in a rotary evaporator. The residual oil was filtered through a column of silica gel, eluting first with carbon tetrachloride and then with chloroform/methanol (9:1). The product was recrystallized from chloroform/petroleum ether (30–60 °C): yield 1.7 g (77%); mp 134–135 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) 8.17 (d, J = 9.08 Hz, 2 H), 7.79 (s, 1 H), 7.63–7.68 (m, 3 H), 7.36–7.45 (m, 2 H), 7.05 (d, J = 9.08 Hz, 2 H), 3.76 (s, 3 H) ppm; ^{13}C NMR ($CDCl_3$, 200 MHz) 162.17, 146.86, 135.06, 133.91, 131.19, 128.62, 127.24, 125.81, 121.72, 115.59, 55.49 ppm; IR (KBr) 3038, 1581, 1561, 1490, 1442, 1301, 1257, 1182, 1027, 895, 822, 737, 522 cm^{-1}; MS (m/e, relative intensity) 374 (M^+ – 2Cl, 17), 366 (1), 307 (4), 244 (100), 194 (20), 142 (2), 102 (51), 63 (19). Anal. Calcd for $C_{15}H_{13}Cl_3OTe$: C, 40.66; H, 2.93. Found: C, 40.78; H, 3.08. [d] Typical experiment: a solution of 1-chloro-1-phenyl-2-[dichloro(p-methoxyphenyl)telluro]ethene (1.55 g, 3.5 mmol) in tetrahydrofuran (30 mL) was treated dropwise with a solution of sodium borohydride (0.14 g, 3.5 mmol) in water (17 mL). The reaction was immediate with gas evolution. After 15 min of stirring at room temperature the mixture was diluted with ether (30 mL) and washed in turns with water, a saturated solution of ammonium chloride, and brine. The organic phase was dried with magnesium sulfate and the solvent evaporated in a rotary evaporator. The residual oil was filtered through a column of silica gel, eluting with petroleum ether: yield 1.07 g (84%); ^{1}H NMR ($CDCl_3$, 200 MHz) 7.76 (d, J = 8.76 Hz, 2 H), 7.18–7.50 (m, 5 H), 7.36 (s, 1 H), 6.79 (d, J = 8.57 Hz, 2 H), 3.76 (s, 3 H) ppm; ^{13}C NMR ($CDCl_3$, 200 MHz), 160,00, 141.03, 140.55, 128.33, 128.11, 127.64, 125.78, 115.47, 109.09, 104.68, 55.09 ppm; IR (KBr) 3057, 2957, 2835, 1882, 1585, 1487, 1284, 1245, 1177, 1029, 750, 514 cm^{-1}; MS (m/e, relative intensity) 374 (M^+, 12), 272 (10), 244 (100), 194 (24), 142 (40), 102 (55), 77 (19). Anal. Calcd for $C_{15}H_{13}ClOTe$: C, 48.40; H, 3.49. Found: C, 48.60; H, 3.57.

The regioisomer shown in eq 1 was formed preferentially in all cases. This conclusion was based on the ^{13}C chemical shifts of the olefinic carbon atom linked to the tellurium atom. These carbon atoms resonate in the range of δ 103–109 for compounds 3. These signals were unambiguously assigned by using two-dimensional ^{1}H–^{13}C chemical shift correlations. The corresponding carbon atoms in compounds 2 exhibit signals in the range of δ 125–128 and are thus deshielded by 19–22 ppm relative to those in compounds 3. We reasoned that the deshielding is exerted

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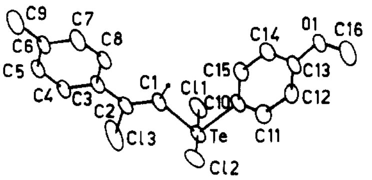
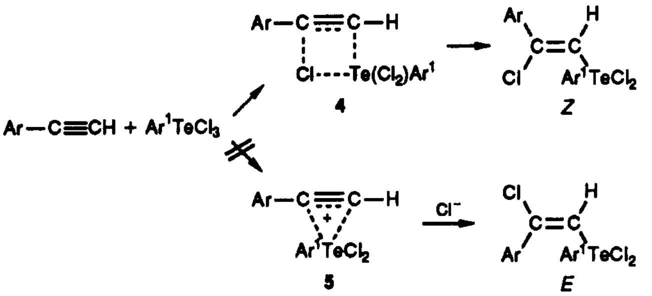


Figure 1. ORTEP drawing of **2b**.

Scheme I



Ar = p-$CH_3C_6H_4$; Ar^1 = p-$CH_3OC_6H_4$

by the inductive effect of the chlorine atoms linked to tellurium. When the chlorine atoms are removed, the C–Te bond polarization is reversed in view of the lower electronegativity of tellurium compared with that of carbon.[14] In this way the carbon atom is negatively polarized and the signal due to this carbon is shifted to higher field. The regiochemistry observed was confirmed by the presence of satellite bands to the signal at δ 125.44 in the ^{13}C NMR spectrum of **2b**. These satellite bands are due to the ^{125}Te–^{13}C coupling. In addition, in the cases where the olefin region of the ^1H NMR spectra of the tellurium dichlorides **2** and tellurides **3** was not crowded, it was possible to observe satellite bands due to ^{125}Te–^1H coupling. X-ray analysis of **2b**[15] confirmed this regiochemistry and also showed that the stereochemistry of this compound is Z (Figure 1). This latter fact is consistent with the four-membered cyclic transition state **4** and not with the telluronium ion intermediate **5**, which should lead to the E isomer (Scheme I). It must be pointed out that the reaction of tellurium tetrachloride with acetylenes and olefins[16] also leads to syn addition products, whereas the addition of aryltellurium trichlorides to olefins gives anti addition products.[16]

The results reported in this communication show that the addition of organyltellurium trichlorides to terminal acetylenes is an efficient method of synthesis of trisubstituted vinylic tellurides.

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Articles

Selective Generation of Various Rhodium Carbonyl Cluster Anions in Aminated Polymers and Their Catalysts for the Water-Gas Shift Reaction and Deoxygenation of Various N–O Bonds

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Aminated polystyrenes were prepared by amination of chloromethylated polystyrenes. Several Rh carbonyl cluster anions could be selectively generated in the aminated polymer with use of $Rh_6(CO)_{16}$. The reaction of $Rh_6(CO)_{16}$ with the aminated polystyrenes at 40 °C under 6 atm of CO gave a dark green polymer involving $[Rh_6(CO)_{15}H]^-$ and $[Rh_6(CO)_{15}]^{2-}$, while $[Rh_{14}(CO)_{25}]^{4-}$ was formed in the polymers at 100 °C. Treatment of the Rh_6 anion species with aqueous KOH solution gave a polymer-bound $[Rh_7(CO)_{16}]^{3-}$ complex. The Rh_6 anion species were catalytically active for the deoxygenation of N–O bonds, e.g., conversion of aliphatic nitro compounds to nitriles, N-oxides to amines, and hydroxylamines to amines. Rh_{14} species could be observed in the water-gas shift reaction. These isolated polymer-bound Rh carbonyl anion complexes were found to be reusable as catalysts for the above reactions.

Much attention has been paid to the metal cluster complexes because of their potential possibility as new catalysts and as the surface model compounds of metal catalysts.[1] We have studied the application of the