

Palladium-catalyzed homocoupling reactions of organic tellurides

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Abstract

Organic tellurides containing a styryl moiety react in acetonitrile to give the corresponding homocoupling products, 1,3-dienes, with moderate to quantitative yields in the presence of a catalytic amount of $\text{Pd}(\text{OAc})_2$ together with AgOAc at 25 °C. In contrast, such homocoupling reactions hardly occur with diaryl, alkyl aryl, dialkyl, and alkynyl aryl tellurides, even at reflux temperature and in the presence of a stoichiometric amount of palladium salt, in disagreement with reported results. The result of cross-over experiments suggests that this homocoupling reaction occurs between an alkenyl telluride and an alkenylpalladium species, the latter being formed via the migration of an alkenyl moiety from Te to Pd (transmetallation).

Keywords: Palladium; Tellurium; Homocoupling; Organic tellurides; Chalcogenide

1. Introduction

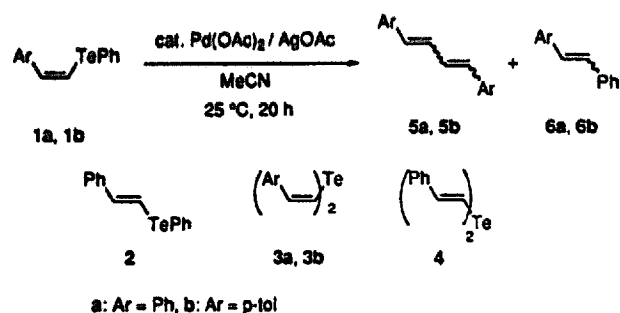
We have previously reported, in communication form, that the treatment of distyryl or phenyl styryl tellurides with a stoichiometric amount of lithium chloropalladate (Li_2PdCl_4) gives the homocoupling products 1,4-diphenyl-1,3-butadienes [1]. During our continuing studies it was clarified that the cross-coupling reaction of these alkenyl tellurides as well as diaryl tellurides with alkenes proceeded catalytically with palladium in the presence of silver acetate (AgOAc) [2]. We then applied this catalytic system to the homocoupling of styryl tellurides and found that the reaction also proceeded catalytically with palladium. It was also disclosed that the homocoupling hardly occurred with other organic tellurides, such as diaryl, alkyl aryl, dialkyl and alkynyl aryl ones, even in the presence of a stoichiometric amount of palladium salt and at higher temperature. This result does not agree with that reported by Barton et al. [3] on the palladium-mediated homocoupling of some of these tellurides, although their detailed experimental conditions are not available. We report here the details of this catalytic homocoupling reaction together with some mechanistic considerations.

2. Results and discussion

2.1. Palladium-catalyzed homocoupling reactions of phenyl styryl tellurides and distyryl tellurides

Treatment of (Z)-phenyl styryl telluride (**1a**) with a stoichiometric amount of Li_2PdCl_4 (a mixture of two equivalents LiCl and one equivalent PdCl_2 to **1a**) in acetonitrile at 25 °C for 20 h afforded the isomeric 1,4-diphenyl-1,3-butadienes (**5a**) in 73% yield (E,E/E,Z/Z,Z 20/52/28). When the amount of palladium(II) salt was reduced to one twentieth, the product yield dropped sharply as expected. However, when AgOAc was added to this reaction system [2,4], the product yield became high and the reaction proceeded catalytically with palladium(II) salt. Although we have shown previously that a stoichiometric amount of palladium(II) acetate ($\text{Pd}(\text{OAc})_2$) reacts with styryl tellurides to give the corresponding styryl acetates [1], it was eventually disclosed that the catalytic use of $\text{Pd}(\text{OAc})_2$ together with AgOAc as reoxidant afforded only the dienes **5a** with highest yields (Scheme 1). Methanol could replace acetonitrile as solvent, but product yields were poor in benzene and tetrahydrofuran (THF). Typical results are shown in Table 1. The characteristic feature of this catalytic reaction is the favorable formation of a Z,Z isomer of **5a**, the stereochemistry (Z-isomer) of the starting telluride being largely retained. Formation of

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Scheme 1.

only a low yield of stilbenes (**6a**) clearly shows that a vinyl moiety is much more labile for this reaction than a phenyl moiety attached to the same tellurium atom. This may be explained by a more facile transmetalation of Te with Pd at the vinylic carbon than at the aryl carbon, in agreement with the result observed in the Pd-catalyzed carbonylation reaction of organic tellurides [5,6].

Next, these catalytic conditions were applied to several other styryl tellurides (**1b**–**4**) (Table 1). All the tellurides reacted smoothly to give the corresponding dienes **5**, where the selectivity for *Z,Z*- and *E,E*-isomers in the products was high from **1** and **3** (*Z*-isomer) and **2** and **4** (*E*-isomer) respectively, as expected. However, compared with homocoupling of other vinylmetal compounds such as Hg [7], Si [8], and B [9] (highly retentive cross-coupling was also observed with alkenylboron compounds; see for example Ref. [10]), where the stereochemistry of the starting compounds was almost com-

pletely retained, the stereoselectivity was lower in the case of vinyl tellurides. It has been reported by Barton et al. [3] that some organic tellurides (R₂TeR') react with a stoichiometric amount of Pd(OAc)₂ in the presence of triethylamine in acetonitrile at 65°C to give only homocoupling products (R–R'). When we applied their reaction system to **1a**, the products consisted of both isomeric mixtures of **5a** (major) and **6a** (minor) together with a small amount of styryl acetates, in sharp contrast with the sole formation of **6a** expected from their result. Since the formation of palladium(0) and its interaction with a telluride were proposed under their conditions, we carried out the coupling of **1a** in the presence of Pd(PPh₃)₄ and again obtained a mixture of **5a** and **6a**. These results, together with those applied to **3a** and **4**, are also shown in Table 1.

In order to obtain some information on the reaction pathway, a cross-over experiment using equal amounts of **3a** and **3b** was carried out in acetonitrile under three different conditions, as shown in Table 1, using cat. Pd(OAc)₂/AgOAc, Pd(OAc)₂/Et₃N and Pd(PPh₃)₄. The products were 1,4-diphenyl-1,3-butadienes **5a**, 1-phenyl-4-*p*-tolyl-1,3-butadienes **7**, and 1,4-di-*p*-tolyl-1,3-butadienes **5b**, and their yields and product ratios were not much different from each other under the three conditions: 40–46% (**5a**/**7**/**5b** 18–32/45–52/27–30) (Scheme 2). The compounds **5a** and **5b** are the expected homocoupling products from **3a** and **3b** respectively, while the compounds **7**, which are the main compounds, are surely derived from cross-coupling between **3a** and

Table 1
Coupling reaction of styryl tellurides ^a

Telluride	Pd salt (equiv.) ^b	Additive (equiv.) ^b	Solvent	Product yields (%) ^c	
				5 (EE/EZ/ZZ)	6 (E/Z)
1a	Li ₂ PdCl ₄ (2) ^d	—	MeCN	73 (20/52/28)	0
1a	Li ₂ PdCl ₄ (0.1) ^d	—	MeCN	6 (0/0/100)	0
1a	Li ₂ PdCl ₄ (0.1) ^d	AgOAc (2)	MeCN	61 (19/0/81)	7 (90/10)
1a	Pd(OAc) ₂ (0.1)	AgOAc (2)	MeCN	83 (22/1/77) [70]	9 (87/13)
1a	Pd(OAc) ₂ (0.1)	AgOAc (2)	MeOH	80 (26/2/72)	7 (84/16)
1a	Pd(OAc) ₂ (0.1)	AgOAc (2)	benzene	13 (0/7/93)	3 (52/48)
1a	Pd(OAc) ₂ (0.1)	AgOAc (2)	THF	9 (0/10/90)	2 (50/50)
1a	Pd(OAc) ₂ (1) ^e	Et ₃ N (2)	MeCN	56 (23/72/5)	19 (76/24) ^f
1a	Pd(PPh ₃) ₄ (1)	—	MeCN	39 (8/65/26)	37 (11/89)
1b	Pd(OAc) ₂ (0.1)	AgOAc (2)	MeCN	69 (26/11/63)	21 (70/30)
2	Pd(OAc) ₂ (0.1)	AgOAc (2)	MeCN	47 (41/31/28)	9 (56/44)
3a	Pd(OAc) ₂ (0.1)	AgOAc (2)	MeCN	75 (20/19/61)	—
3a	Pd(OAc) ₂ (1)	Et ₃ N (2)	MeCN	30 (32/61/7)	— ^f
3b	Pd(OAc) ₂ (0.1)	AgOAc (2)	MeCN	40 (38/8/54)	—
4	Pd(OAc) ₂ (0.1)	AgOAc (2)	MeCN	60 (50/40/10)	—
4	Pd(OAc) ₂ (1) ^e	Et ₃ N (2)	MeCN	47 (56/38/6)	— ^f

^a All reactions were carried out at 25°C for 20 h using **1a** (0.5–1 mmol) and solvent (10 ml) unless otherwise noted.

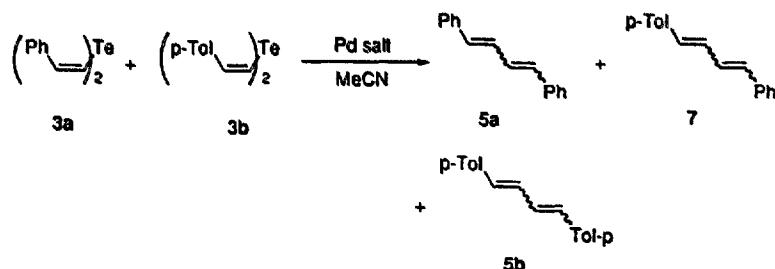
^b Equivalent to **1a**.

^c GLC yield; 0.5 mol equiv. of **5a** to **1a** and 1 mol equiv. of **6a** to **1a** correspond to 100% respectively. Isolated yield in square brackets.

^d Prepared in situ from 1 equiv. PdCl₂ and 2 equiv. LiCl.

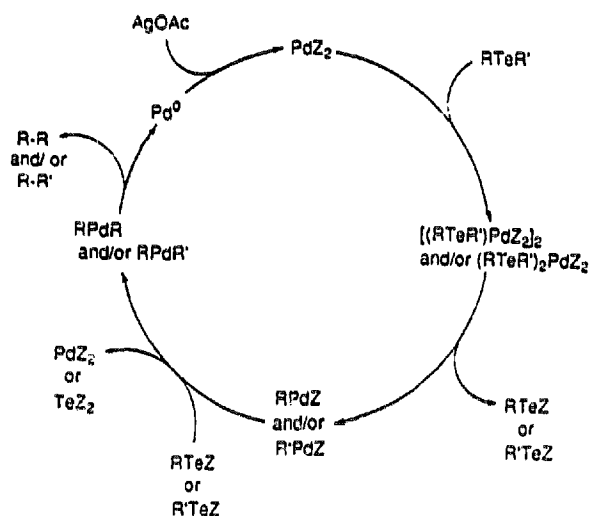
^e At 82°C for 2 h.

^f Other product: styryl acetate (PhCH=CHOAc), 8–10%.



Scheme 2.

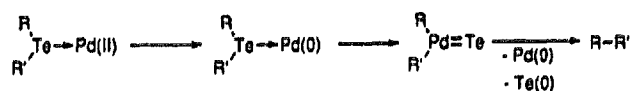
3b. The result clearly indicates that an alkenylpalladium species derived from either 3a or 3b reacts with another 3a or 3b to give 7. By considering this result as well as the reaction scheme proposed at palladium-catalyzed cross-couplings between similar tellurides and alkenes [2], we propose Scheme 3 as a catalytic cycle of this homocoupling reaction. Namely, the formation of an organic telluride–palladium(II) complex is followed by alkenyl or aryl migration to give aryl- or alkenylpalladium species (transmetalation), which react with an organic telluride to give diorganopalladium. Its reductive elimination furnishes homocoupling products and palladium(0), the latter being oxidized with AgOAc to palladium(II), to complete the catalytic cycle. The stereochemistry of the products was not controlled, in contrast to the carbonylation case [5,6] as described above, probably because the reaction of the alkenyl- or arylpalladium species with an organic telluride is slow to allow the *cis/trans* isomerization in organopalladium species. In contrast, the formation of the cross-coupling product 7, as well as the major formation of 5a from 1a under Barton et al.'s conditions, indicates that the reaction pathway (Scheme 4) proposed by them [3] should not be the major one in Pd(0)-mediated coupling.



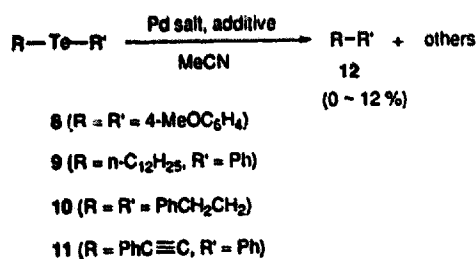
Scheme 3.

2.2. Attempts at homocoupling reactions of diaryl, alkyl aryl, dialkyl and alkynyl aryl tellurides

We have already reported that palladium(II)-mediated aromatic coupling occurs with diaryltellurium dichlorides in acetic acid [11] and with aryltellurium trichlorides in acetonitrile in the presence of carbon monoxide [12]. Aiming at the development of a more facile and general method for the coupling reaction using organotellurium compounds, the palladium-catalyzed homocoupling reaction described in a previous section was next applied to a variety of organic tellurides such as bis(4-methoxyphenyl) telluride 8, dodecyl phenyl telluride 9, bis(2-phenethyl) telluride 10, and phenyl phenylethynyl telluride 11 (Scheme 5). As shown in Table 2, however, the expected homocoupling reaction hardly occurred and the formation of a small amount of alkene was observed in the cases of 9 and 10. Since a palladium-mediated facile ligand coupling of some of these tellurides was reported [3], the homocoupling reaction was attempted in our hands under reported reaction conditions (1 equiv. $\text{Pd}(\text{OAc})_2$ /2 equiv. Et_3N at 65 °C for 7 h under argon) and also under slightly modified conditions (at 82 °C for 2–10 h under argon or air) for comparison. As a result, only 8–10% yields of 4,4'-dimethoxybiphenyl and tolane and 1,4-diphenyl-1,3-butadiene were obtained as homocoupling products from 8 and 11 respectively and, further, alkenes were the main products from 9 and 10. By the use of a stoichiometric amount of $\text{Pd}(\text{PPh}_3)_4$ the results were nearly the same and homocoupling hardly occurred again (Table 2). The formation of alkenes such as 1-dodecene from 9 and styrene from 10 can be explained by successive reactions of a telluride–palladium complex formation, subsequent formation of alkylpalladium(II) species, and a well-known β -hydride elimination. Anyway, palladium-catalyzed and -mediated homocoupling of these tellurides did not proceed well in



Scheme 4.



Scheme 5.

our hands, and we have not yet been successful in developing a new and general catalytic method for ligand coupling of organic tellurides. The reason why we could not reproduce the experiments of Barton et al. is not yet clear.

3. Experimental details

¹H (270 MHz) and ¹³C (67.5 MHz) NMR spectra were measured on a JEOL GSX-270 spectrometer as solutions in CDCl₃. Melting points were determined on a Yanaco MP-S3 micro melting point apparatus and are uncorrected. GLC analyses were performed on a Hitachi 163 instrument (1 m × 3 mm stainless steel column packed with 20% PEG on Shimalite) and a Shimadzu GC-14A instrument (25 m HiCap-CBP-10-S25 capillary column) with flame-ionization detectors and N₂ as carrier gas. Column chromatography on SiO₂ was per-

Table 2
Coupling reaction of tellurides 8–11^a

Telluride	Condition ^b	Products and yield (%) ^c	
		12	Others
8	A	1	—
8	B	8–10	—
8	C	12	—
9	A	0	1-dodecene (4), biphenyl (17)
9	B	0	1-dodecene (33), biphenyl (13)
9	C	0	1-dodecene (21), biphenyl (18)
10	A	0	styrene (3)
10	B	0	styrene (74)
10	C	0	styrene (29)
11	A	5	— ^d
11	B	2–3	1,4-diphenyl-1,3-butadiene (6–7), biphenyl (3)
11	C	0	— ^d

^a All reactions were carried out using telluride (0.5–1 mmol) and MeCN (10 ml).

^b Condition A: Pd(OAc)₂ (0.1 equiv. to telluride), AgOAc (2 equiv.), at 25°C for 20 h. Condition B: Pd(OAc)₂ (1 equiv.), Et₃N (2 equiv.), at 65°C for 7 h and/or at 82°C for 2–10 h. Condition C: Pd(PPh₃)₄ (1 equiv.), at 25°C for 20 h.

^c GLC yield: 1 mol equiv. of 12 and alkene and 0.5 mol equiv. of biphenyl and 1,4-diphenyl-1,3-butadiene to the employed telluride correspond to 100% and 50% respectively.

^d Not determined precisely; at most < 10% yield.

formed with Wakogel C-300 (hexane and hexane/ethyl acetate as eluents). Elemental analyses were performed at the Microanalytical Center of Kyoto University. Commercially available organic and inorganic compounds were used without further purification. Authentic samples of 5a, 5b and 7 were prepared by treatment of the corresponding vinyl bromides with vinyl borate esters in the presence of palladium salt according to the reported method [13]. The retention times of each compound in GLC (25 m capillary column) increased in the following order: (E,Z)-5a < (Z,Z)-5a < (E,Z)-7 < (E,E)-5a < (Z,Z)-7 < (E,E)-7 < (E,Z)-5b < (Z,Z)-5b < (E,E)-5b. Other authentic samples such as *trans*- and *cis*-stilbenes, *trans*- and *cis*-1-phenyl-2-p-tolyethylene, 4,4'-dimethoxybiphenyl, 1-phenyldodecane, n-tetracosane, 1,4-diphenylbutane, tolane, 1,4-diphenyl-1,3-butadiene, biphenyl, 1-dodecene and styrene for GLC analysis were commercial reagents. The following organotellurium compounds were prepared by the reported method respectively: (Z)-PhCH=CHTePh 1a [14]; (Z)-p-TolCH=CHTePh 1b [6]; (E)-PhCH=CHTePh 2 [6]; (Z,Z)-(PhCH=CH)₂Te 3a [1]; (E,E)-(PhCH=CH)₂Te 4 [15]; bis(4-methoxyphenyl) telluride 8 [16]; 1-dodecyl phenyl telluride 9 [15]; bis(2-phenethyl) telluride 10 [17]; phenyl phenylethynyl telluride 11 [18]. Several related new styryltellurium compounds are reported here for convenience. (E,E)-(PhCH=CH)₂TeCl₂, prepared by treatment of 4 with SO₂Cl₂ (90% yield), white solid, m.p. 100–101°C (from EtOH). ¹H NMR δ 7.38–7.54 (10H, m), 7.47 (2H, d, J = 15.8 Hz), 7.84 (2H, d, J = 15.8 Hz). ¹³C NMR δ 121.6 (=C–Te), 127.9 (d), 129.0 (d), 130.5 (d), 134.6 (s), 147.2 (=C–Ph). Anal. Found: C, 47.46; H, 3.49. C₁₆H₁₄Cl₂Te Calc.: C, 47.48; H, 3.49%. (Z,Z)-(PhCH=CH)₂TeCl₂, prepared by treatment of 3a with SO₂Cl₂ (80% yield), white needle, m.p. 162–163°C (from EtOH). ¹H NMR δ 7.41–7.52 (12H, m), 7.67 (2H, d, J = 7.2 Hz). ¹³C NMR δ 127.7 (d), 128.2 (d, =C–Te), 129.4 (d), 129.9 (d), 136.7 (s), 142.5 (d, =C–Ph). Anal. Found: C, 47.51; H, 3.45%. (Z,Z)-(PhCH=CH)₂Te(OAc)₂, prepared by reaction of the corresponding dichloride with AgOAc (60% yield), white needle, m.p. 128–130°C (from hexane/CHCl₃). ¹H NMR δ 1.57 (6H, s), 7.01 (2H, d, J = 10.2 Hz), 7.66 (2H, d, J = 10.2 Hz), 7.33–7.54 (10H, m). ¹³C NMR δ 21.2 (q), 125.3 (d, =C–Te), 127.4 (d), 129.0 (d), 129.3 (d), 137.0 (s), 144.6 (d, =C–Te), 176.4 (s, C=O). Anal. Found: C, 53.15, H, 4.44. C₂₀H₂₀O₄Te Calc.: C, 53.15, H, 4.46%.

3.1. Preparation of (Z,Z)-bis(p-methylstyryl) telluride 3b

In a 100 ml round-bottomed flask containing a magnetic stirring bar were placed sodium hydride (60%, oil

dispersion) (3.05 g, 76.3 mmol) (washed twice with hexane and dried under vacuum) and tellurium powder (4.80 g, 37.6 mmol) under N_2 . Anhydrous N,N-dimethylformamide (DMF) (30 ml) was added to the flask at room temperature by a syringe, and the mixture was stirred at 140°C for 0.5 h, during which time the color of the heterogeneous solution turned from purple to pale yellow. After it had been cooled, a solution of (Z)-p-methyl-2-bromostyrene (10.2 g, 51.8 mmol), prepared by alkaline treatment of the bromination product of (E)-p-methylcinnamic acid [19], in DMF (5 ml) was added to the resulting mixture by a syringe at room temperature, and then the mixture was stirred at 120°C for 1 h. The resulting mixture was filtered through Celite to remove gray precipitates which were washed with diethyl ether (200 ml). The filtrate combined with the ether washing was washed with aqueous NH_4Cl solution and then with brine. The ether layer was dried over $MgSO_4$. Evaporation of the solvent left a red-orange liquid, which was subjected to column chromatography on silica gel (Wakogel C-300) with hexane as eluent to afford an orange oil of (Z,Z)-bis(p-methylstyryl) telluride **3b** (2.63 g, 7.27 mmol, 19.3% yield). 1H NMR δ 2.34 (6H, s), 6.93 (2H, d, $J = 10.3$ Hz), 7.1–7.3 (8H, m), 7.40 (2H, d, $J = 10.3$ Hz). ^{13}C NMR δ 21.3 (q), 106.0 (s), 107.8 (d), 127.4 (d), 129.2 (d), 136.0 (s), 137.3 (d). Anal. Found: C, 59.98; H, 4.80. $C_{18}H_{18}Te$ Calc.: C, 59.73; H, 5.01%.

3.2. A typical experimental procedure of the coupling reaction

Into a two-necked 50 ml round-bottomed flask containing $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), $AgOAc$ (167 mg, 1.00 mmol) and (Z)-phenyl styryl telluride **1a** (153.8 mg, 0.50 mmol) was added dry acetonitrile (10 ml). After the homogeneous reaction mixture had been stirred at 25°C for 20 h, the solid was filtered. The filtrate was poured into brine (200 ml) and extracted with diethyl ether (3 $\times$ 50 ml). GLC determination of the ether extract with diphenylmethane as internal stan-

dard showed the presence of 0.208 mmol (83% yield) of 1,4-diphenyl-1,3-butadienes **5a** (EE/EZ/ZZ 22/1/77) and 0.045 mmol (9% yield) of stilbenes **6a** (E/Z 87/13). Isolation by column chromatography on SiO_2 (Wakogel C-300; hexane and hexane/EtOAc (9/1) as eluents) afforded 36.1 mg (0.175 mmol, 70% yield) of **5a**.

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