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Styryl coupling vs. styryl acetate formation in reactions of styryl tellurides with palladium(II) salts

Sakae Uemura ^{*1}, Hidetaka Takahashi and Kouichi Ohe

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611 (Japan)

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Abstract

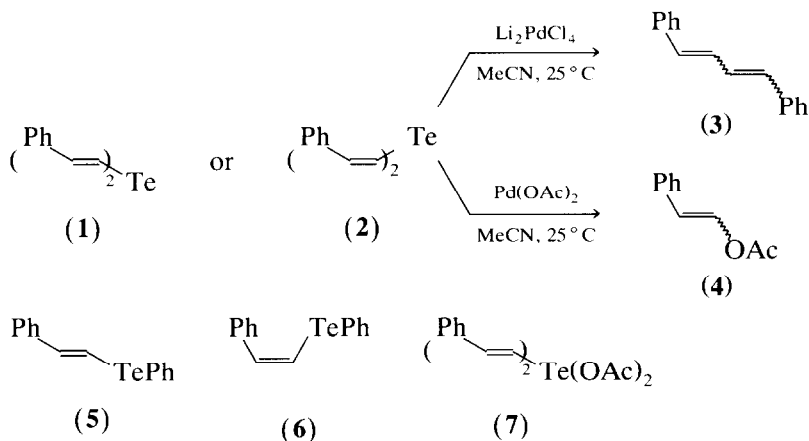
In sharp contrast to the expected formation of a telluride-palladium complex, the treatment of either (*E,E*)- and (*Z,Z*)-distyryl tellurides (**1** and **2**) or (*E*)- and (*Z*)-styryl phenyl tellurides (**5** and **6**) with Li_2PdCl_4 in acetonitrile at 25°C results in the formation of stereoisomeric 1,4-diphenylbuta-1,3-dienes, whereas the treatment of **1** and **2** with $\text{Pd}(\text{OAc})_2$ produces styryl acetates solely or mainly.

It has been known previously that various dialkyl and diaryl tellurides can form monomeric and/or dimeric complexes with palladium(II) salts such as $(\text{R}_2\text{Te})_2\text{PdCl}_2$ and/or $[(\text{R}_2\text{Te})\text{PdCl}_2]_2$ (R = alkyl, aryl) [1]. During our attempts to prepare such complexes from dialkenyl or alkenyl aryl tellurides and palladium(II) salts, in the course of the study of the Pd-promoted carbonylation of organic tellurides [2], we unexpectedly encountered other reactions than the expected complex formation; the coupling of alkenyl moieties and the substitution of a tellurium moiety by an acetoxyl group [3].

When (*E,E*)-distyryl telluride (**1**) (1 mmol) was treated with lithium chloropalladate (2 mmol; added as a mixture of PdCl_2 and LiCl) in acetonitrile (10 ml) at 25°C for 20 h, an isomeric mixture of 1,4-diphenylbuta-1,3-diene (**3**) was produced in 61% yield (by GLC, isolated yield 55%, 1 mmol as 100%) in a ratio of *E,E*/*E,Z*/*Z,Z* = 56/36/8. An aliquot of the reaction mixture after 5 h showed the presence of **3** having the same isomer ratio as that obtained after 20 h, and even when the reaction was carried out at reflux temperature for 2 h, the isomer ratio of **3** obtained was nearly the same. These facts show that there is no isomerization between three isomers under the reaction conditions employed [4*]. Similar treatment of (*Z,Z*)-distyryl telluride (**2**) [5*] at 25°C for 20 h also produced **3** in 69% isolated yield in a ratio of *E,E*/*E,Z*/*Z,Z* = 22/47/31, different from that of **1**. All cases gave black precipitates, elemental analysis of which revealed

¹ Present address: Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto 606 (Japan).

* Reference number with asterisk indicates a note in the list of references.



the absence of C and H, suggesting the precipitates to be either palladium, tellurium or Pd–Te. In the cases of (*E*)-styryl phenyl telluride (**5**) and its stereoisomer (**6**) the compound **3** was obtained as well, together with a small amount of stilbene, in 41 and 73% yield (by GLC; 0.5 mmol as 100%) in similar isomer ratios compared with those of **1** and **2**, respectively.

However, the treatment of **1** (0.5 mmol) with palladium(II) acetate (1 mmol) in acetonitrile at 25°C produced styryl acetate (**4**) (*E/Z* = 100/0) almost solely in 70% yield (1 mmol as 100%). Similarly, from **2** the acetate **4** (*E/Z* = 18/82) was formed pure in 58% yield. Although diorganyl tellurides may be easily oxidized, a possible path for **4** via the initial formation of distyryltellurium diacetate (**7**) and Pd^0 by the interaction of **1** with $\text{Pd}(\text{OAc})_2$ was excluded by the results of separate experiments [7*]. On the other hand, similar treatment of diphenyl telluride and didodecyl telluride with $\text{Pd}(\text{OAc})_2$ resulted in the formation of $(\text{Ph}_2\text{Te})_2\text{Pd}(\text{OAc})_2$ (69%) [8*] and 1-dodecene (56%) respectively, none of phenyl acetate and dodecyl acetate being produced.

A recent report by Barton et al. [9] on the formation of coupled products $\text{R}^1\text{--R}^2$ from R^1TeR^2 ($\text{R}^1, \text{R}^2 = \text{alkyl, aryl}$) by treatment with a stoichiometric amount of Pd^0 prompted us, for comparison, to treat vinylic tellurides, **1**, **2**, and **6** under similar reaction conditions. It was expected that (*E,E*)-**3** and (*Z,Z*)-**3** would be formed stereospecifically from **1** and **2** respectively and (*Z*)-stilbene produced solely from **6**. However, the treatment of **1** and **2** (1 mmol) with $\text{Pd}(\text{OAc})_2$ (1 mmol)/ Et_3N (2 mmol) in refluxing acetonitrile for 2 h (Barton's conditions) produced an isomeric mixture of **3** in 47 and 36% yield, respectively (by GLC; 1 mmol as 100%) together with **4** in 8–10% yield, the isomer ratio of **3** being roughly the same as ours in both cases. The reaction proceeded smoothly even at 25°C giving an almost similar isomer ratio of **3** from **1** as that obtained at reflux temperature. Similar treatment of **6** also produced an isomeric mixture of **3** in 56% yield (by GLC; 0.5 mmol as 100%), whereas the yield of the expected coupled product, stilbene, was only 19% (*E/Z* = 76/24). Typical results of all these reactions, including the isomer ratio of products, are shown in Table 1.

The comparison of the isomer distribution in **3** as well as the product distribution in our case with those under Barton's conditions suggests the presence of

Table 1

Reactions of styryl tellurides with Pd salts in acetonitrile ^a

Te compound	Pd salt	Temp (°C)	Time (h)	Products, yields (%) ^b and isomer ratio ^c	
				3 (<i>E,E</i> / <i>E,Z</i> / <i>Z,Z</i>)	4 (<i>E</i> / <i>Z</i>)
1	Li ₂ PdCl ₄	25	20	61 (56/36/8)	—
1	Li ₂ PdCl ₄	82	2	48 (59/35/6)	—
1	Pd(OAc) ₂	25	20	trace	70 (100/0)
1	Pd(OAc) ₂ /Et ₃ N	25	20	65 (59/36/5)	16 (100/0)
1	Pd(OAc) ₂ /Et ₃ N	82	2	47 (56/38/6)	8 (100/0)
5	Li ₂ PdCl ₄	25	20	41 (63/35/2)	— ^d
2	Li ₂ PdCl ₄	25	20	69 ^e (22/47/31)	—
2	Pd(OAc) ₂	25	20	0	58 ^e (18/82)
2	Pd(OAc) ₂ /Et ₃ N	82	2	36 (32/61/7)	10 ^f
6	Li ₂ PdCl ₄	25	20	73 (20/52/28)	— ^g
6	Pd(OAc) ₂ /Et ₃ N	82	2	56 (23/72/5)	8 ^{f,h}

^a Telluride 0.5–1 mmol; MeCN 10 ml; telluride/Li₂PdCl₄ or Pd(OAc)₂ = 1/2; telluride/Pd(OAc)₂/Et₃N = 1/1/2. ^b GLC yield. ^c Determined by GLC. ^d Other product; stilbene, 7% (*E*/*Z* = 84/16). ^e Isolated yield. ^f Stereochemistry is not determined. ^g Other product; stilbene, trace. ^h Other product; stilbene, 19% (*E*/*Z* = 76/24).

intrinsically similar reaction pathways between the two. Although the details are not yet known, compound **3** may be produced by cross-coupling between the starting telluride and a styryl-palladium(II) species (PhCH=CHPdZ) formed by transmetallation between Te and Pd after complex formation. It is not yet clear whether the reaction involves a distyryl-palladium(II) intermediate and its reductive elimination as suggested by Barton et al., but, if so, we might expect more stereospecific formation of **3**.

One possible scheme for **4** seems to be the retentive substitution of a styryltellurium moiety by Pd(OAc)₂ to produce a styryl-palladium(II) acetate followed by stereospecific reductive elimination as has been postulated in the Pd(OAc)₂-catalyzed conversion of vinylmercury(II) compounds into enol acetates [10].

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References and notes

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- K. Ohe, H. Takahashi, S. Uemura and N. Sugita, *J. Organomet. Chem.*, 326 (1987) 35; *idem*, *J. Org. Chem.*, 52 (1987) 4859.
- Partly presented at the 53rd Annual Meeting of the Chemical Society of Japan at Nagoya (October 1986) and at the 35th Symposium on Organometallic Chemistry, Japan at Osaka (November 1988).
- We confirmed separately that (*E,E*)-1,4-diphenylbuta-1,3-diene is completely recovered intact after treating it with palladium metal and either lithium chloride or triethylamine in acetonitrile at reflux for 2 h.
- For preparation of the tellurides **1**, **5**, and **6**, see ref. 6. The compound **2** was similarly prepared as **1** from Na₂Te and (*Z*)-β-bromostyrene in 57% isolated yield as a pale yellow solid; m.p. 48–49°C (from hexane). ¹H NMR (CDCl₃): δ 7.01 (d, 2H, *J* = 10.4 Hz), 7.46 (d, 2H, *J* = 10.6 Hz), 7.22–7.42

- (m, 10H) ppm. ^{13}C NMR (CDCl_3): δ 108.9 (=C–Te), 127.4 (d), 127.6 (d), 128.5 (d), 137.4 (=C–Ph), 138.8 (s) ppm. Anal. Found: C, 57.62, H, 4.21. $\text{C}_{16}\text{H}_{14}\text{Te}$ calc.: C, 57.56; H, 4.23%.
- 6 K. Ohe, H. Takahashi, S. Uemura and N. Sugita, *Nippon Kagaku Kaishi*, (1987) 1469.
- 7 The compound **7** was prepared by the reaction of the corresponding dichloride with AgOAc in refluxing benzene, the dichloride [a white needle, m.p. 100–101°C (from EtOH)] being prepared by the treatment of **1** with SO_2Cl_2 .
- 7**: a white solid, m.p. 119–120°C (from hexane/ CHCl_3). ^1H NMR δ (ppm) 2.08 (s, 6H), 7.23 (d, 2H, $J = 16.4$ Hz), 7.54 (d, 2H, $J = 16.4$ Hz), 7.25–7.51 (m, 10H) ppm. ^{13}C NMR: δ 22.2 (q), 120.9 (d, =C–Te), 127.5 (d), 128.8 (d), 130.0 (d), 135.3 (s), 146.8 (d, =C–Ph), 177.3 (s, OCO) ppm. Anal. Found: C, 52.89, H, 4.57. $\text{C}_{20}\text{H}_{20}\text{O}_4\text{Te}$ calc.: C, 53.15; H, 4.46%. It was stable in MeCN at 25°C even in the presence of Pd powder or $\text{Pd}(\text{PPh}_3)_4$ and completely recovered intact after 20 h.
- 8 A yellow solid: m.p. 132–134°C (dec). Anal. Found: C, 42.48, H, 3.38. $\text{C}_{28}\text{H}_{26}\text{O}_4\text{Te}_2\text{Pd}$ calc.: C, 42.67; H, 3.33%.
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