

Preliminary communication

REACTION OF DIAZONIUM SALTS WITH TRANSITION METALS

XII *. PALLADIUM-CATALYZED ARYLDESTANNYLATION OF α -STYRYLSTANNANES BY ARENEDIAZONIUM SALTS

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(Received June 20th, 1986)

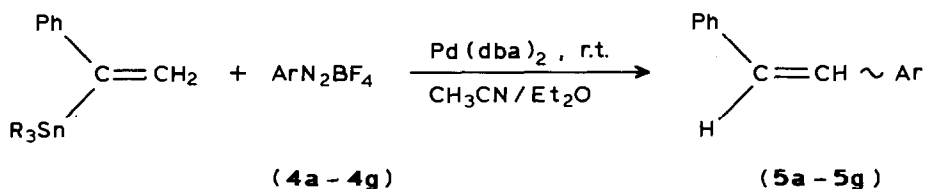
Summary

Under palladium(0) catalysis, $\text{Ph}(\text{R}_3\text{Sn})\text{C}=\text{CH}_2$ ($\text{R} = \text{Me, Et and Bu}$) easily reacted with ArN_2BF_4 ($\text{Ar} = \text{XPh, X} = \text{H, 4-Me, 4-I, 4-MeCO, 4-EtOCO, 3-NO}_2$ and 4-NO_2) and selectively produced (*Z*)- $\text{PhCH}=\text{CHAr}$ but not $\text{Ph}(\text{Ar})\text{C}=\text{CH}_2$. An addition-elimination mechanism instead of the transmetallation from tin to palladium is postulated for this unusual regiochemistry.

Organostannanes have been conveniently utilized in the palladium-catalyzed cross-coupling with organic halides [1–4]. Arenediazonium salts (ArN_2X) can be also alkylated by organostannanes under palladium catalysis [5]. These synthetically useful transformations of organostannanes including alkenylstannanes rely on the transmetallation from tin to palladium as a key step. In the course of our research on the palladium-catalyzed reaction of ArN_2X , we found an interesting aryldestannylation of α -styrylstannanes.

In the presence of catalytic bis(dibenzylideneacetone)palladium(0) ($\text{Pd}(\text{dba})_2$), tributyl- β -styrylstannanes (*E/Z* 62/38) easily reacted with PhN_2BF_4 at room temperature to give stilbene (*E/Z* 63/37) with retention of its geometry as expected by the transmetallation step [1,2]. Unexpectedly the reactions of trialkyl- α -styrylstannanes (1–3) with ArN_2BF_4 (4) did not give α -arylated styrenes but selectively produced (*Z*)-stilbenes ((*Z*)-5) (eq. 1, Table 1).

* For part XI see ref. 8.



(1 , R = Me ;
 2 , R = Et ;
 3 , R = Bu) .

(a ; Ar = Ph , b ; Ar = 4-MePh , c ; Ar = 4-IPh ,
 d ; Ar = 4-MeCOPh , e ; Ar = 4-EtOCOPh ,
 f ; Ar = 3-NO₂Ph , g ; Ar = 4-NO₂Ph)

The bulky substituents on tin give better selectivity. Since the use of excess 4 caused considerable isomerization of (*Z*)-5, a 5–10% excess of 1–3 to 4 should be used to obtain (*Z*)-5. In the absence of 1–3, (*Z*)-5a is easily isomerized to (*E*)-5a under the present reaction conditions. Since the isomerization does not proceed in the absence of the palladium catalyst, the H–Pd species ([H–Pd]⁺ BF₄[–]) may play a crucial role. Alkenylstannanes react with H–Pd species to regenerate Pd⁰ (eq. 2, see also Scheme 1) [6].

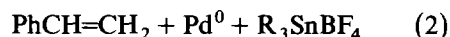
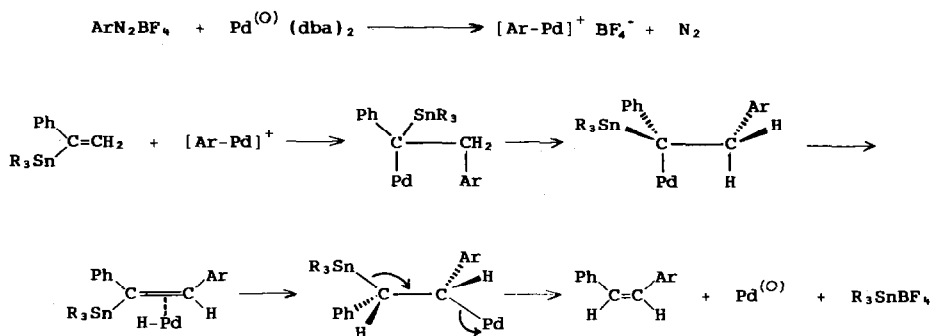


TABLE 1

PALLADIUM-CATALYZED ARYLDESTANNYLATION OF Ph(R₃Sn)C=CH₂ (1–3) BY ArN₂BF₄ (4) (eq. 1) ^a

1–3	4	Pd(dba) ₂ (mol %)	Time (min)	Yields ^b (%)	Products (% , ratio) ^c	
					(<i>E</i>)-5	(<i>Z</i>)-5
1	4a	10	– ^d	97	40	60
2	4a	10	– ^d	95	18	82
3	4a	10	– ^d	95	17	83
3	4a	5	20	90	18	82
3 ^e	4a	4	20	(98) ^e	65	35
3	4b	5	15	97	7	93
3	4c	5	120	86	8	92
3	4d	5	60	80(60) ^f	17	83
3	4e	5	60	97(70) ^f	7	93
3	4f	5	120	54	8	92
3	4g	5	60	60(42) ^f	16	84

^a The reactions were carried out with 2 mmol of 4, 2.2 mmol of 1–3 and Pd(dba)₂ in a mixed solvent of CH₃CN (12 ml) and Et₂O (8 ml) at room temperature under nitrogen, and were stopped by addition of 0.5 ml of Et₃N after gas evolution ceased. ^b Isolated yields based on 4. ^c Determined by GLC. ^d Gas evolution ceased within 10 min, but the mixture was stirred for 1 h. ^e Two mmol of 4a and 1.7 mmol of 3 were used, and the yield was based on 3. ^f Isolated yields of (*Z*)-5.



SCHEME 1.

The present, high, but unexpected regioselectivity can be explained by an addition-elimination mechanism, which has been proposed for the palladium catalyzed arylation of alkenylsilanes [7,8], as shown in Scheme 1.

The reaction of zero-valent palladium with **4** easily generates the arylpalladium species (Ar-Pd) [5,9]. Steric and electronic effects of Ph and R₃Sn on **1-3** determine the regiochemistry of the addition of Ar-Pd to **1-3**. The relative bulkiness of Ph and R₃Sn (R₃Sn > Ph) responds to the stability of the adducts, and hence to the selective formation of (*Z*)-**5**.

Since (*Z*)-**5** can be easily separated from (*E*)-**5** by column chromatography (silica gel CCl₄/CHCl₃), the present reaction provides a convenient procedure for the preparation of (*Z*)-stilbenes bearing a wide variety of substituents including halogens, ester, ketone and nitro groups.

References

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- 6 Styrene generated by the reaction described in eq. 2 can be arylated by **4** under palladium catalysis. However, the arylation yields exclusively (*E*)-**5** [10].
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