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Note

Arylation of alkenes by the palladium(II) acetate–dialkyl sulfide system

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Abstract

Reactions of the palladium(II) acetate–dialkyl sulfide system with phenyl substituted ethylenes in aromatic compounds, carried out at 70 °C for 5 h, afford arylated alkenes. Comparing the yields obtained by the system with the previously reported ones, it was found that the system is a more convenient arylating reagent for alkenes

Key words: Catalysis, Arylation; Palladium complexes; Alkene complexes

Introduction

Carbon–hydrogen bond activation of hydrocarbons is an attracting theme in organometallic chemistry [1]. We have been challenging this theme by use of the palladium(II) acetate–dialkyl sulfide system. Up to date, we have reported the reactions of arenes or ketones with the palladium(II) acetate–dialkyl sulfide system, resulting in the formation of the diaryltripalladium(II) complexes $[Pd_3Ar_2(\mu\text{-}O_2CMe)_4(SR_2)_2]$ (Ar = Ph,*p*-xylyl) [2] and the cyclic tetranuclear palladium(II) complexes containing an *o*-phenylene group $[Pd_4(\mu\text{-}o\text{-}C_6H_4)_2(\mu\text{-}O_2CMe)_4(\mu\text{-}SR_2)_2]$ [3] or the β-carbonylmethylpalladium(II) complexes $[PdCl(CH_2COR)(Me_2bpy)]$ [4], respectively. Moreover, we have reported the oxidative coupling of benzene by the system, which was performed under milder reaction conditions at 70 °C with higher activity compared with palladium(II) acetate alone [5]. In connection with these works, we have investigated the reactions of alkenes with the system in aromatic compounds, i.e., arylation of alkenes, and report the results here.

Experimental

Palladium(II) acetate was prepared according to the procedure of Wilkinson and co-workers [6]. Solvents were dried by the usual methods and distilled, then degassed by a stream of nitrogen or oxygen before use. Other reagents were used without purification.

General procedure for arylation of alkenes by the palladium(II) acetate–dialkyl sulfide system

Normal reaction conditions are as follows. In a 100 cm^3 two-necked flask, palladium(II) acetate (0.050 g, 0.223 mmol), an appropriate amount of dialkyl sulfide and the aromatic compound (10 cm^3) were placed under nitrogen or oxygen atmosphere. The mixture was heated at 70 °C under nitrogen or oxygen for the appropriate reaction time. After cooling to ambient temperature, analysis of the products were carried out on a Shimadzu GC-14A gas chromatograph with a flame ionization detector on a BP-1 (50 m × 0.25 mm) capillary column. Yields of (*E*)-stilbene, triphenylethylene, tetraphenylethylene and biphenyl were determined using hexadecane as an internal standard. Yields of mono-*p*-xylylated and mono-mesitylated compounds of styrene were determined using the calibration curve for hexadecane-(*E*)-stilbene. Yields of mono-*p*-xylylated and mono-mesitylated compounds of (*E*)-stilbene, and di-*p*-xylylated compounds of styrene were determined using the calibration curve for hexadecane-triphenylethylene. Yields were the averaged values of three or four experiments. Identity of (*E*)-stilbene, triphenylethylene, tetraphenylethylene and biphenyl was confirmed by comparison of the GLC retention times with authentic samples. *p*-Xylylated and mesitylated alkenes and 1,4-diphenyl-1,3-butadiene were confirmed by GC/MS on a Shimadzu GCMS-QP2000 instrument: $PhCH{=}CH(2,5\text{-}Me_2C_6H_3)$ *m/z* 208 (M^+), $Ph(2,5\text{-}Me_2C_6H_3)C{=}CH(2,5\text{-}Me_2C_6H_3)$ *m/z* 312 (M^+), $PhCH{=}CH(2,4,6\text{-}Me_3C_6H_2)$ *m/z* 222 (M^+), $PhCH{=}CPh(2,5\text{-}Me_2C_6H_3)$ *m/z* 284 (M^+), $PhCH{=}CPh(2,4,6\text{-}Me_3C_6H_2)$ *m/z* 298 (M^+) and $(PhCH{=}CH)_2$ *m/z* 206 (M^+).

Results and discussion

Reactions of styrene with the palladium(II) acetate–dialkyl sulfide system in benzene (phenylation of styrene)

Reactions of styrene with the palladium(II) acetate–dialkyl sulfide system were performed at 70 °C for

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5 h in benzene Effects of sulfides and molar ratios of $\mathrm{Pd(O_2CMe)_2/SPr^i_2}$ towards the yields of (*E*)-stilbene, a phenylation product of styrene, were investigated under N_2 atmosphere with the 1/1 molar ratio of styrene/$\mathrm{Pd(O_2CMe)_2}$. These results (Table 1) showed that the most promising sulfide is $\mathrm{SPr^i_2}$ and the best molar ratio of $\mathrm{Pd(O_2CMe)_2/SPr^i_2}$ is 1/0.5, which were the same results as those observed in the coupling reaction of benzene by the system [5]. It is noted that in the absence of sulfide the yield of (*E*)-stilbene is very low (2%).

When the reaction was performed under O_2 atmosphere with a 1/1 molar ratio of styrene/$\mathrm{Pd(O_2CMe)_2}$, triphenylethylene was obtained in 120% yield (based on $\mathrm{Pd(O_2CMe)_2}$) in addition to (*E*)-stilbene (Table 2, Run no. 1). This fact indicated that (*E*)-stilbene derived from the phenylation of styrene undergoes a further phenylation with benzene and that the phenylation proceeds catalytically with respect to palladium under atmospheric pressure of oxygen. Concerning the phenylation of styrene by palladium(II) acetate, Fujiwara *et al.* reported that (*E*)-stilbene was obtained in 90% yield in benzene in the presence of acetic acid (0.24 mol equivalent to benzene) under reflux for 8 h in air [7]. Shue also reported that the phenylation of styrene proceeded catalytically by use of mild oxygen pressure (2.07×10^6 Pa) in benzene at 80 °C for 2.5 h without additives to give (*E*)-stilbene in 300% yield [8]. Our system is more convenient than the previously reported methods stated above in the sense that the phenylation of styrene proceeds smoothly even at 70 °C just by addition of the sulfide and catalytically just under atmospheric pressure of oxygen.

TABLE 1 Effects of sulfide and molar ratio of $\mathrm{Pd(O_2CMe)_2}$–$\mathrm{SR_2}$ on the yields of (*E*)-stilbene by the $\mathrm{Pd(O_2CMe)_2}$–$\mathrm{SR_2}$ system[a]

$\mathrm{SR_2}$	Molar ratio of $\mathrm{Pd(O_2CMe)_2/SPr^i_2}$	Yield of (*E*)-stilbene[b] (%)
$\mathrm{SBu^t_2}$	1:1/2	28
$\mathrm{SPr^i_2}$	1:2	50
	1:1	59
	1:2/3	58
	1:1/2	63
$\mathrm{SBu^i_2}$	1:1/2	51
$\mathrm{SPr_2}$	1:1/2	51
$\mathrm{SEt_2}$	1 1/2	52
$\mathrm{SPh_2}$	1:1/2	8
		2

[a] Reaction conditions $\mathrm{Pd(O_2CMe)_2}$, 0.233 mmol, $\mathrm{PhCH{=}CH_2}$, 0 223 mmol; benzene, 10 $\mathrm{cm^3}$, at 70 °C for 5 h under N_2 atmosphere. [b] Determined by GLC analyses Based on $\mathrm{Pd(O_2CMe)_2}$

When the ratios of styrene/$\mathrm{Pd(O_2CMe)_2}$ were increased up to 10/1 or 20/1, the yield of (*E*)-stilbene was over 100% based on $\mathrm{Pd(O_2CMe)_2}$, but dimerization of styrene was found to take place simultaneously (Table 2, Run nos. 2 and 3). It is probable that excess styrene blocks the coordination site for benzene to interact with palladium, which lowers the formation of phenylpalladium species and on the contrary accelerates the dimerization of styrene.

Reactions of styrene with the palladium(II) acetate–diisopropyl sulfide system in p-xylene and mesitylene (p-xylylation and mesitylation of styrene)

p-Xylylation and mesitylation of styrene were performed with a 1/0.5/1 molar ratio of $\mathrm{Pd(O_2CMe)_2/SPr^i_2}$/styrene at 70 °C for 5 h. In the absence of sulfide, the yield of the *p*-xylylated or mesitylated styrene was very low under both N_2 and O_2 atmosphere (Table 2, Run nos. 6, 7, 11 and 12). On the contrary, by this system arylation of styrene proceeded smoothly even under N_2 atmosphere to give (*E*)-2,5-dimethylstilbene of (*E*)-2,4,6-trimethylstilbene in 79 or 45% yield, respectively (Table 2, Run nos. 4 and 9) These yields are much higher than those previously reported (47 and 9%, respectively) by Fujiwara and co-workers [9]. Moreover, under O_2 atmosphere (*E*)-2,5-dimethylstilbene underwent further *p*-xylylation to give a mixture of (*E*)- and (*Z*)-2,5,2′,5′-tetramethyltriphenylethylene [(*E*)/(*Z*) = 5.5/1] in 26% yield, whereas (*E*)-2,4,6-trimethylstilbene did not undergo further mesitylation (Table 2, Run nos. 5 and 10). When *p*-xylylation was carried out with 10/1 molar ratio of styrene/$\mathrm{Pd(O_2CMe)_2}$, (*E*)-2,5-dimethylstilbene was obtained almost quantitatively with respect to palladium, but the dimerization of styrene also occurred at the same time (Table 2, Run no. 8).

Reactions of (E)-stilbene or triphenylethylene with the palladium(II) acetate–diisopropyl sulfide system in benzene, p-xylene or mesitylene

Phenylation, *p*-xylylation and mesitylation of (*E*)-stilbene were carried out with a 1/0.5/1 molar ratio of $\mathrm{Pd(O_2CMe)_2/SPr^i_2}$/(*E*)-stilbene at 70 °C, and the results are summarized in Table 3. In the case of the phenylation of (*E*)-stilbene, triphenylethylene was obtained quantitatively by reaction under O_2 atmosphere for 5 h. However, it was found that a coupling reaction of benzene occurred at the same time, giving biphenyl in 43% yield. As for the *p*-xylylation of (*E*)-stilbene, almost quantitative 2,5-dimethyltriphenylethylene was obtained after 1 day under O_2 atmosphere without the formation of bi(*p*-xylyl), though the product was a mixture of the isomers (*E*) and (*Z*). A slow reaction was observed in the case of mesitylation of (*E*)-stilbene and even after 1 day under O_2 atmosphere only a 17% yield of 2,4,6-trimethyltriphenylethylene was obtained.

When the alkene is much bulkier, as is in the case of phenylation of triphenylethylene, a coupling reaction

TABLE 2 Arylation of styrene by the $Pd(O_2CMe)_2$–SPr^i_2 system[a]

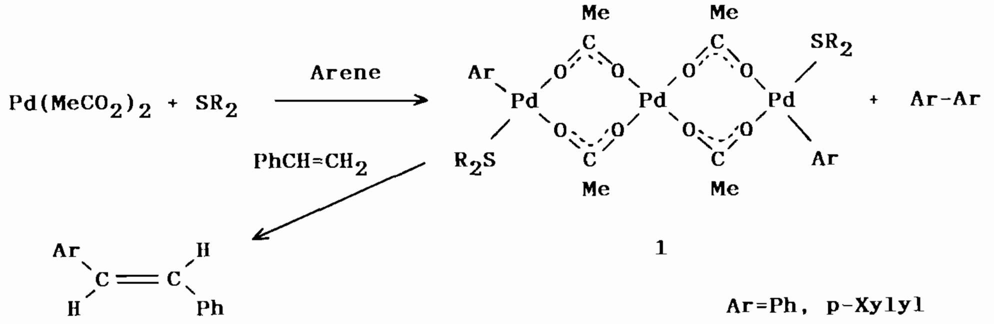
Aromatics	Run no	Molar ratio of $PhCH{=}CH_2/Pd(O_2CMe)_2$	Yield[b] (%)			Atmosphere
			PhCH=CHAr	PhArC=CHPh	$(PhCH{=}CH)_2$[c]	
Benzene						
(Ar = Ph)	1	1:1	16	120	0	O_2
	2	10 1	113	0	21[d]	O_2
	3	20·1	102	0	62[e]	O_2
p-Xylene						
(Ar = *p*-xylyl)	4	1·1	79	0	0	N_2
	5	1 1	60	26[f]	0	O_2
	6[g]	1:1	4	0	0	N_2
	7[g]	1:1	10	0	0	O_2
	8	10·1	102	0	24[h]	O_2
Mesitylene						
(Ar = mesityl)	9	1 1	45	0	0	N_2
	10	1·1	50	0	0	O_2
	11[g]	1:1	2	0	0	N_2
	12[g]	1·1	5	0	0	O_2
	13	10.1	39	0	24[i]	O_2

[a] Reaction conditions. $Pd(O_2CMe)_2$, 0.223 mmol; SPr^i_2, 0.111 mmol, aromatic compound 10 cm^3, at 70 °C for 5 h. [b] Determined by GLC analyses. Based on $Pd(O_2CMe)_2$. [c] 1,4-Diphenyl-1,3-butadiene, see text [d] Isomer ratio of (1*E*, 3*E*)/(1*E*, 3*Z*) was 7/1. [e] Isomer ratio of (1*E*, 3*E*)/(1*E*, 3*Z*) was 8/1 [f] (*E*)/(*Z*) = 5.5/1. [g] Without SPr^i_2. [h] Isomer ratio of (1*E*, 3*E*)/(1*E*, 3*Z*) was 15/1. [i] Isomer ratio of (1*E*, 3*E*)/(1*E*, 3*Z*) was 7/1.

TABLE 3. Arylation of (*E*)-stilbene by the $Pd(O_2CMe)_2$–SPr^i_2 system[a]

Aromatics	Reaction time (h)	Yield[b] (%)			Atmosphere
		PhCH=CPhAr	PhArC=CPhAr	Ar–Ar	
Benzene	5	77	0	3	N_2
	5	99	trace	43	O_2
p-Xylene	5	74[c]	0	0	O_2
	24	95[c]	0	0	O_2
Mesitylene	24	17[c]	0	0	O_2

[a] Reaction conditions: $Pd(O_2CMe)_2$, 0.223 mmol; SPr^i_2, 0.111 mmol; aromatic compound 10 cm^3, at 70 °C. [b] Determined by GLC analyses. Based on $Pd(O_2CMe)_2$. [c] Molar ratio of (*E*)/(*Z*) was 2/1.



Scheme 1. Formation of diaryltripalladium(II) complexes and their reactions.

of benzene rather than phenylation of triphenylethylene proceeded predominantly using our system to give biphenyl and tetraphenylethylene in 139 and 1% yield, respectively, based on $Pd(O_2CMe)_2$. It was reported that a similar reaction carried out in a benzene/acetic acid mixed solvent in air using only $Pd(O_2CMe)_2$ gave a 17% yield of tetraphenylethylene but formation of biphenyl was not mentioned [7].

Previously, we reported that the reaction of the palladium(II) acetate–dialkyl sulfide system with benzene or *p*-xylene gave the diaryltripalladium(II) complex (**1**), together with the formation of the coupling product, biphenyl or bi(*p*-xylyl) [2] (Scheme 1). Moreover, we demonstrated as a model reaction for arylation of alkenes that styrene reacted with **1** to afford (*E*)-stilbene or (*E*)-2,5-dimethylstilbene quantitatively [2]. Taking these facts into consideration, it is plausible that initially the system reacts with arenes to give the diaryltripalladium(II) complexes, followed by the insertion of alkenes which were activated by coordination to palladium, and finally the subsequent β-hydrogen elimination afforded the aryl-substituted alkenes. However, when the incoming alkenes were bulkier, such as triphenylethylene, coordination of the alkenes would be restricted and so the coupling reactions proceeded predominantly.

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