

AROMATIC SUBSTITUTION OF STYRENE-PALLADIUM CHLORIDE COMPLEX, II
EFFECT OF METAL ACETATE⁽¹⁾

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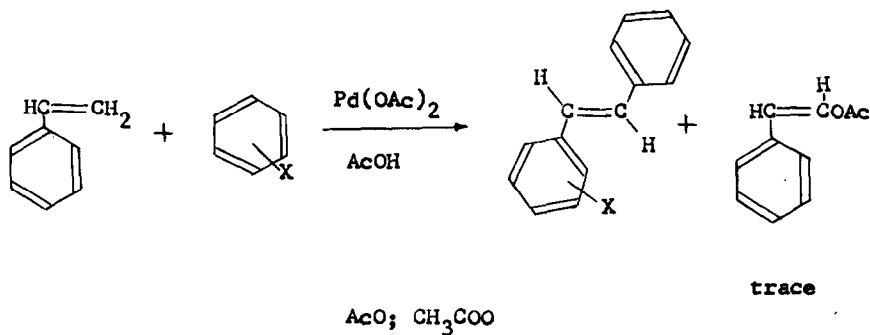
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In the previous communication⁽¹⁾, we reported a novel method of synthesizing stilbene derivatives by substitution of aromatic compounds for hydrogen on the double bond of styrene-palladium chloride complex (I).

We have found that the aromatic substitution of styrene also takes place almost quantitatively (90-97% yield) in the presence of palladium acetate instead of the styrene complex I or styrene complex I with a large amount of metal acetates.

The present communication deals with this method of preparing stilbene derivatives by the aromatic substitution of styrene.



In a solution of 3.36 g of styrene (equal mol. equivalent to palladium acetate), 340 ml of dry benzene and 80 ml of acetic acid, 7.21 g of palladium acetate was dissolved, and the mixture was refluxed with continued stirring for 8 hours. The precipitated palladium metals were filtered off and the filtrate was washed with water and then dried over sodium sulfate. Evaporation of the benzene gave 5.24 g of the crude crystalline material IIa, mp 115-120° (90% yield based on styrene), and 0.052 g of liquid III, bp 118-121° at 10 mm (1%). Recrystallization of IIa from ethanol gave 5.11 g of white crystals of trans-stilbene⁽²⁾, mp 122-123° (88%). The crude liquid substance III was distilled carefully to give 0.046 g of pure liquid substance, C₁₀H₁₀O₂, bp 119-121° at 10 mm, which was shown to be β-acetoxy-styrene through comparison of the infrared spectrum and retention time of vpc with those of an authentic sample⁽³⁾.

In case of toluene, trans-p-methylstilbene (58%), trans-o-methylstilbene (3%) and a trace amount of β-acetoxy-styrene III were obtained. Similarly, p-xylene affords trans-2,5-dimethylstilbene (47%) and the acetate III (trace).

An excess amount of sodium acetate with complex I⁽⁴⁾ also gave trans-stilbene in high yield. Thus 3.01 g of styrene complex I was refluxed with 113 ml of dry benzene, 27 ml of acetic acid and 16.4 g (20 mol. equivalent to palladium chloride) of sodium acetate. On treating the reaction mixture as usual, trans-stilbene was obtained in 97% yield (based upon styrene of complex I), with a trace amount of acetate III. In table 1, the relationship between the amount of sodium acetate and the yield of trans-stilbene IIa, acetate III and IV⁽²⁾ is shown. The yield of trans-stilbene increases with the increase of the amount of sodium acetate, and when 20 mol. equivalent of sodium acetate are used, styrene is substituted with benzene almost quantitatively.

Table 1 also shows that α-phenylethyl acetate IV, is obtained as byproducts with the unsaturated acetate III, when the amount of sodium acetate is less than 2 mol. equivalent to palladium chloride. This fact indicates that palladium chloride is an active catalyst for the addition of acetic acid to styrene.

Furthermore, when sodium acetate was used with palladium chloride, trans-stilbene was obtained in good yield. Thus in a solution of 120 ml of dry benzene, 40 ml of acetic acid, 2.87 g of palladium chloride and 26.8 g of sodium acetate,

Table 1. Effect of sodium acetate

NaOAc ^a	Complex I (g)	Benzene (ml)	AcOH ^b (ml)	Stilbene IIa	Yield (%)	
					Acetate III	Acetate IV ⁽²⁾
0.36	9.1	340	80	25	1.5	8.0
2.0	4.0	150	36	86	4.7	1.8
7.2	9.1	340	80	90	1	0
20	3.0	113	27	97	1	0

^aSodium acetate; mol. equivalent to palladium chloride

^bAcetic acid

1.70 g (equal mol. equivalent to palladium chloride) of styrene was dissolved, and the mixture was heated at reflux with continued stirring for 8 hours. On treating the reaction mixture as mentioned above, trans-stilbene was obtained in 79% yield together with a trace amount of acetate III. Similarly, when potassium acetate (7.2 mol. equivalent to palladium chloride) was used in lieu of sodium acetate, trans-stilbene was formed in 26% yield.

These results show that the metal acetates play an important role in this reaction. It might be that after the chloride anion is abstracted from the palladium chloride by the metal cation (Na^+ , K^+), the palladium metal coordinates to the acetate anion which is weaker ligand than the chloride anion, thus increasing the ability of the palladium metal to coordinate with styrene, and therefore it becomes possible for this aromatic substitution of styrene to take place in such high yield. Further experiments concerning this interesting reaction are in progress, and the details of this reaction will be reported in a forthcoming paper.

REFERENCES

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carried out as shown in the preceding communication⁽¹⁾.

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