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The Palladium-catalyzed Phenylation of Enol Esters with Iodobenzene

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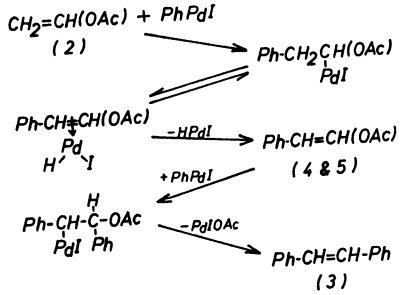
Synopsis. The palladium-catalyzed phenylation of olefins with iodobenzene has been extended to enol esters. In the presence of triethylamine and a catalytic amount of palladium acetate, vinyl acetate is phenylated with iodobenzene to produce, mainly, stilbene, accopanied by small amounts of (*E*)- and (*Z*)-styryl acetates.

Recently, the palladium-catalyzed substitution of vinylic hydrogen by aryl and vinyl halides has received wide attention.[1-5] Meanwhile, Heck[6] has reported the reaction of enol esters with the organo-palladium species generated from an arylmercury(II) compound and palladium salts. We are, therefore, intrigues by the palladium-catalyzed reaction of enol esters with iodobenzene (**1**) and wish to report herein the results of a study of this reaction.

Table 1 shows the results of the phenylation of enol esters with **1**. The reaction of vinyl acetate (**2**) with **1** gave stilbene (**3**) as the main product and (*E*)- and (*Z*)-styryl acetates (**4** and **5**) as the minor products. Since neither styrene nor acetophenone enol ester was found in the reaction mixture and since, in addition, a mixture of **4** and **5** reacted with **1** to give **3** under the same conditions, the compound **3** appears to be formed by the secondary phenylation of **4** and **5**, as despicted in Scheme 1. (Scheme 1).

The phenylation of isopropenyl acetate (**6**) gave three isomers of the diphenylated propene derivatives (**7**, **8**, and **9**) and two isomers of (*E*)- and (*Z*)-2-acetoxy-1-phenyl-1-propene (**10** and **11**). It has been reported[6] that the Heck reaction of **2** with phenylmercury(II) salt gave **4** and **5** as the main products and **3** and styrene as the minor products, while the Heck reaction of **6** afforded a mixture of **10**, **11**, and 2-acetoxy-3-phenyl-1-propene. The results obtained here indicate that the phenylation of **2** and **6** with **1** favors the formation of diphenylated olefin compounds more than the Heck reaction of **2** and **6**.



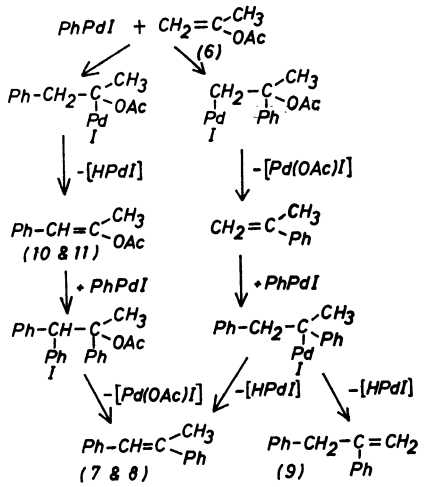
Scheme 1.

A common mechanism has been proposed for the arylation of olefins with aryl halides.[2,3] In the phenylation of **6** with **1**, the formation of 2,3-diphenyl-1-propene (**9**) may require that the phenylpalladium group is added to the double bond in both possible directions

TABLE 1. PHENYLATION OF ENOL ESTERS WITH IODOBENZENE (**1**)

Enol ester	Product, bp or mp°C, (lit)	Yield[a] %
CH_2=CH(OAc) (**2**)	Biphenyl, mp 68—69 (mp 69—70[b])	3
	(*E*)-Stilbene (**3**), mp 124, (mp 123—124[c])	52
	(*E*)-Styryl acetate (**4**)	10
	(*Z*)-Styryl acetate (**5**), bp of the mixture of **4** and **5** 95—120/2.5 Torr (bp 87—112/1.5 Torr[d])	2
Ph-CH=CH(OAc) (**4** and **5**, **4**/**5**=7/1)	Biphenyl	3
	(*E*)-Stilbene (**3**)	58
CH_2=CCH_3(OAc) (**6**)	Biphenyl	24
	(*E*)-2,2-Diphenyl-1-propene (**7**), mp 78—79 (mp 79—79.5[e])	21
	(*Z*)-1,2-Diphenyl-1-propene (**8**), mp 47—48 (mp47—48[e])	8
	2,3-Diphenyl-1-propene (**9**), bp 162—165/14 Torr (bp 81—83/0.12 Torr[e])	2
	(*E*)-2-Acetoxy-1-phenyl-1-propene (**10**), bp 102—105/3 Torr (bp 112—116/5 Torr[f])	10
	(*Z*)-2-Acetoxy-1-phenyl-1-propene (**11**), bp 102—105/3 Torr (bp 112—116/5 Torr[f])	2
CH_2=C(OAc)Ph (**12**)	Biphenyl	36
	(*E*)-Stilbene (**3**)	25
	1,2-Diphenyl-1-acetoxyethene (**13**),mp 104—106, (mp 102—106[g])	20

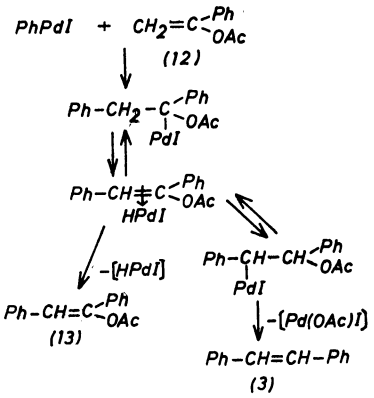
a) The yields are based upon the iodobenzene (**1**) used are determined by gas chromatography. b) E. Muller and T. Topel *Ber.*, **72**, 273 (1939). c) R. L. Shrine and A. Bergrr, *Org. Synth.*, Coll. Vol. III, 786 (1965). d) R. F. Heck, *Organometal. Chem. Syn.*, **1**, 455 (1972). e) D. H. Hunter and D. J. Cram. *J. Am. Chem. Soc.*, **86**, 5478 (1964). f) H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, **34**, 2324 (1969). g) C. V. Gheorghin, *Chem. Abstr.*, **17**, 1559, (1923).



Scheme 2.

(Scheme 2).

The phenylation of acetophenone enol acetate (**12**) gave **3** and 1,2-diphenyl-1-acetoxyethene (**13**). The formation of **3** may require three intermediate steps, namely, the initial elimination, a readdition of the palladium hydride in the reverse direction, and another elimination of Pd(OAc)I, as shown in Scheme 3.



Scheme 3.

Experimental

Materials. Iodobenzene, vinyl acetate, and isopropenyl acetate of a commercial grade were used without further purification. The preparation of the following compounds has already been reported: (*E*)- and (*Z*)-styryl acetates[7] and acetophenone enol acetate.[9]

General Procedure for The Phenylation of Enol Acetate. A mixture of 2.04 g (10 mmol) of **1**, 12 mmol of enol acetate, 1.21 g (12 mmol) of triethylamine, 0.022 g (0.1 mmol) of palladium acetate, and 0.524 g (0.2 mmol) of triphenylphosphine in acetonitrile (10—15 ml) was heated in a sealed tube flushed with nitrogen at 100 °C for 8 h. The products were isolated by diluting the cooled reaction mixtures with water and ether. The ether phase was separated, washed several times with water, dried over anhydrous magnesium sulfate, and concentrated. The products were generally analyzed by gas chromatography on a 1 m SE 30 (5% on celite) column with a Hitachi K-53 gas chromatograph, and identified by comparing the retention time on the gas chromatogram and the IR and NMR spectra with those of an authentic sample. The reactions carried out are listed in Table 1.

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