# Addition of Benzene to α-Substituted Chalcones with Palladium(II) Acetate

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*Summary* Some α-substituted chalcones reacted with benzene and acetic acid in the presence of palladium acetate to give the benzene-adducts, 1,1-diphenyl-2-substituted-2-benzoylethanes, together with the usual phenylated compounds.

In recent years, extensive studies of the arylation of olefins by use of palladium salts have been reported.[1] In the course of our studies[2] on the phenylation of styrenes by Moritani–Fujiwara arylation, a novel addition reaction was found in which benzene added to the carbon–carbon double bond of some α-substituted chalcones. When α-benzoylchalcone (Ia) was refluxed for 24 h with an equimolar amount of palladium acetate, benzene, and acetic acid, (IIa) was obtained as the major product (52%),† together with a small amount of the usual phenylated product (IIIa) (8%). The structure of (IIa) was determined by its n.m.r., i.r., u.v., and mass spectra and elemental analysis.

$$\underset{\text{(I)}}{\text{PhCH=CR(COPh)}} \xrightarrow[\text{Pd(OAc)}_2]{\text{C}_6\text{H}_6\text{–AcOH}}$$

$$\underset{\text{(II)}}{\text{Ph}_2\text{CHCHR(COPh)}} + \underset{\text{(III)}}{\text{Ph}_2\text{C=CR(COPh)}}$$

a, R = COPh; b, R = $\text{NO}_2$; c, R = $\text{CO}_2\text{Et}$

To our knowledge, this is the first example of addition of benzene to a carbon–carbon double bond being brought about by Pd salts. (IIa) can be regarded both as the benzene-adduct of (Ia) and the reduction product of (IIIa). However, reduction of the carbon–carbon double bond of (IIIa) to (IIa) did not occur under the reaction conditions used. When (Ia) was treated with $\text{C}_6\text{D}_6$ and $\text{MeCO}_2\text{D}$, under similar conditions, the hexadeuterio-compound (IIa′) was obtained. The structure of (IIa′) was determined by its n.m.r. spectrum. These findings indicate that (IIIa) was not an intermediate in the formation of (IIa) from (Ia).

$$\text{(Ia)} \xrightarrow[\text{Pd(OAc)}_2]{\text{C}_6\text{D}_6\text{–AcOD}} \underset{\text{(IIa}'\text{)}}{\text{C}_6\text{D}_5\text{CHPhCD(COPh)}_2}$$

Likewise, α-nitrochalcone (Ib) and α-ethoxycarbonylchalcone (Ic) reacted with benzene and acetic acid in the presence of palladium acetate to afford the corresponding benzene-adducts, (IIb) (20%) and (IIc) (12%), respectively, plus the usual phenylated products, (IIIb) (5%) and (IIIc) (57%).

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† Yields are of isolated, purified products.

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[2] K. Yamamura, *J.C.S. Perkin I*, 1975, 988; K. Yamamura and S. Watarai, *Bull. Chem. Soc. Japan*, 1975, **48**, 3757.