Tetrahedron Letters No.35, pp. 3863-3865, 1968. Pergamon Press. Printed in Great Britain.

AROMATIC SUBSTITUTION OF OLEFIN. IV
REACTION WITH PALLADIUM METAL AND SILVER ACETATE

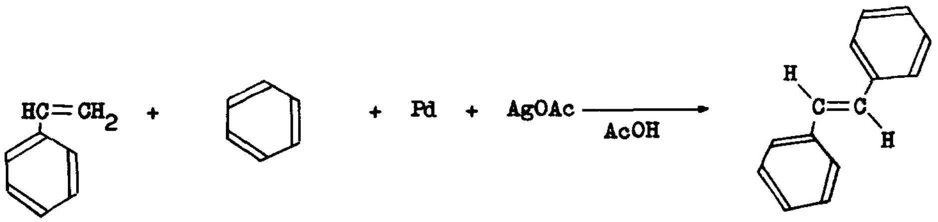
Yuzo Fujiwara, Ichiro Moritani, Masaoki Matsuda and Shiichiro Teranishi

Department of Chemistry, Faculty of Engineering Science,
Osaka University, Machikaneyama, Toyonaka, Osaka, Japan

(Received in Japan 11 May 1968; received in UK for publication 7 June 1968)

In previous papers,[1)] we reported a novel substitution reaction between styrene and benzene derivatives in the presense of palladium(II) salts such as palladium(II) acetate, giving stilbene derivatives by substitution of aromatic compounds for hydrogen on the double bond of styrene. This is a convenient new method for the introduction of phenyl groups into the olefinic C-atom.

In this reaction, however, an equal amount of palladium(II) salts to olefin is necessary and the palladium(II) salt is reduced to metal in the course of this reaction. Therefore it is of interest to investigate whether palladium(II) salts can act catalytically in this substitution reaction.



AcO; CH_3COO

We have found that this reaction proceeds catalytically when silver acetate is used with palladium(II) acetate and that even palladium metal can afford phenyl-substituted olefins if silver acetate is introduced together.

In a solution of 50 ml of dry benzene, 12 ml of acetic acid and 1.30 g of styrene(12.5 mmoles) were added palladium(II) acetate(5 mmoles) and silver acetate(25 mmoles), and the mixture was heated at reflux with continued stirring for 8 hours. The resulting mixture was filtered and the filtrate was washed free from acetic acid with 5% aq. sodium bicarbonate, followed by water. The benzene layer was dried over anhydrous magnesium sulfate. After evaporation of the benzene, the residue was chromatographed on activated alumina. Elusion with petroleum ether gave the crude crystalline material Ia, mp 115-120°(138% yield based on palladium), and elusion with ether yielded the crystals II (11% yield). Recrystallization of the crude Ia from ethanol afforded colourless crystals of trans-stilbene[2) of mp 122-123° and recrystallization of the crude II gave colourless crystalline material of mp 149-150° which was identical with authentic trans,trans-diphenylbutadiene.[3) The yield of trans-stilbene(Ia) increased to ca 200% when 3 mol. equivalent of silver acetate to palladium(II) acetate was used.

Similarly ethylene undergoes this substitution reaction in palladium(II) acetate-silver acetate system. Thus into a stirring solution of dry benzene (100 ml), acetic acid(24 ml), palladium(II) acetate(10 mmoles) and silver acetate(100 mmoles), was bubbled ethylene(40 ml/min.) under reflux for 8 hours. On treating the reaction mixture as usual, there were obtained styrene and trans-stilbene(Ia) in 59% and 75% yields respectively. In case of toluene, p-methylstyrene(37%) and trans-p,p'-dimethylstilbene(Ib;21%)[2) were obtained. These compounds were assigned by comparison with authentic materials.

Furthermore, when palladium metal was used with silver acetate, this substitution reaction also occurs. To a mixture of palladium powder (16.1 mmoles), silver acetate (32.2 mmoles) in 40 ml of acetic acid and 170 ml of dry benzene, styrene (16.1 mmoles) was added, and the mixture was refluxed with continued stirring for 8 hours. After work-up as usual, we obtained trans-stilbene(Ia) in 21% yield.

On the other hand, no stilbene was formed if palladium powder was used without silver acetate or silver acetate without palladium powder. These results indicate that palladium metal is oxidized to palladium(II) which is active for this reaction, by silver acetate. In fact, when palladium metal was treated with silver acetate in acetic acid, the solution became deep red which palladium (II) acetate in acetic acid indicates, and when sodium formate was added to this deep red solution, palladium metal precipitated, suggesting palladium(II) acetate was formed from metal palladium and silver acetate. Therefore, in this palladium (II) acetate-silver acetate system, palladium metal which derives from palladium (II) acetate, being reduced in the course of the reaction, can be oxidized again to palladium(II) which is effective for this aromatic substitution, thus it becomes possible that palladium(II) salts act as a catalyst in this reaction.

In addition to silver acetate, the metal acetate such as cupric is also effective for the oxidizing reagent for palladium metal to palladium(II).

Further experiments concerning this reaction are under current investigation and the details of this reaction will be reported in the full paper.

REFERENCES

1) a) I. Moritani and Y. Fujiwara, Tetrahedron Letters, 1119 (1967); Tetrahedron, **24**, in press.
   b) Y. Fujiwara, I. Moritani, M. Matsuda and S. Teranishi, Tetrahedron Letters, 633 (1968).

2) Assignment of stilbene derivatives described here was carried out as shown in the previous paper.[1-a)]

3) B. B. Corson, ''Organic Syntheses,'' Coll. Vol. II, p. 229 (1943).