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AROMATIC SUBSTITUTION OF STYRENE-PALLADIUM CHLORIDE COMPLEX

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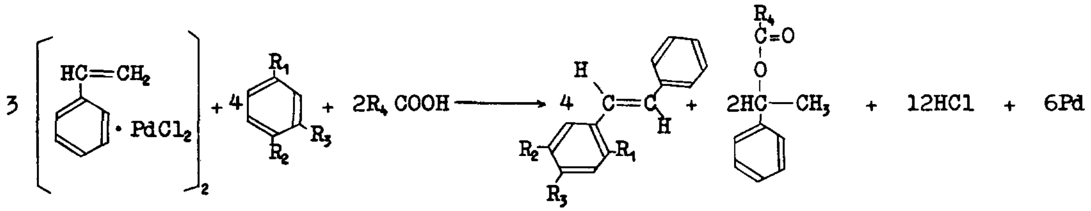
We wish to report here a new synthetic method of stilbene derivatives by the substitution of aromatic compounds to a double bond of styrene-palladium chloride complex (I).

The substitution reaction of an anion to a double bond with olefin-metal complexes is well known. For example, aldehyde derivatives,(1) unsaturated acetic acid derivatives,(2) and unsaturated ethers,(3) are obtained by the nucleophilic attack of water, acetate anion and alkoxy anion to olefin-palladium chloride complexes, respectively. Olefins also give carbonyl compounds, when treated with carbon monoxide with the palladium chloride catalyst.(4)

However, a substitution of aromatic compounds to a double bond by means of olefin-palladium chloride complexes has never been found.



I

IIa: $R_1 = R_2 = R_3 = H$ IIIa: $R_4 = CH_3$

IIb: $R_1 = R_2 = H$, $R_3 = CH_3$ IIIb: $R_4 = CH_2Cl$

IIc: $R_1 = R_2 = CH_3$, $R_3 = H$

In a solution of 340 ml. of dry benzene and 80 ml. of acetic acid, 9.10 g. of styrene complex I(5) was dissolved, and after the deoxydation, the mixture was refluxed with continued stirring for 8 hours in a slow stream of oxygen-free nitrogen. The precipitated palladium metals were removed, and the filtrate was distilled under reduced pressure, to give 1.87 g. of styrene (56% yield based on styrene of I), 0.73 g. of distillate IIIa, b.p. 65-68° at 5 mm., and 1.64 g. of the crystals IIa. Recrystallization of the crude material IIa from petroleum ether gave 1.50 g. of the white crystals IIa, m.p. 122-123° (26% yield). The infrared spectrum of this substance IIa exhibited the characteristic absorption bands at 690, 762 cm^{-1} (mono-sub. benzene) and at 960 cm^{-1} (trans C-H), and the ultraviolet spectrum and chemical properties showed that IIa was *trans*-stilbene (IIa; $R_1 = R_2 = R_3 = H$). The structure of IIa was also confirmed with mixed melting point test with an authentic sample. The crude liquid substance IIIa was separated by vapour phase chromatography to give 0.67 g. of liquid substance, $C_{10}H_{12}O_2$, b.p. 105-107° at 15 mm. (13% yield). This substance was assigned to be phenyl methyl carbinol acetate (IIIa; $R_4 = CH_3$) through comparison of the infrared spectrum and retention time with those of an authentic sample.(6) Therefore, this result suggests that styrene was substituted by benzene. However, it is also probable that phenyl group of stilbene might be derived from the decomposition of styrene, not from benzene itself. This can be eliminated from the following result.

Toluene was used instead of benzene. If the reaction involves a substitution of the solvent molecule, methyl-substituted stilbene should be obtained. On the contrary, if the decomposition of styrene is involved, stilbene should be produced. Complex I was refluxed gently with dry toluene and acetic acid. On treating the reaction mixture as usual, the white crystals IIb, $C_{15}H_{14}$, m.p. 119-120° (25% yield) and acetate IIIa (14% yield) were obtained. This compound IIb was identical in all respects (I.R., U.V.,N.M.R., and mixed m.p. test) with authentic *trans*-p-methyl stilbene(7) (IIb; $R_1 = R_2 = H$, $R_3 = CH_3$).

Thus, this result shows that solvent toluene reacted as a reagent with styrene. Acetate IIIa was given by the addition of acetic acid to styrene.

There is, however, another possibility of the formation of stilbene.

Thus, benzene adds to styrene to form diphenylethane, which is followed by the dehydrogenation with palladium (or palladium chloride).

In order to clarify this subject, diphenylethane was treated in the same condition as the above. The starting material was recovered quantitatively. Moreover, when acetate IIIa was treated with benzene, acetic acid and palladium chloride (and palladium metal), acetate IIIa was also recovered quantitatively. Thus, it is clear that stilbene is formed by the direct substitution of styrene with benzene. Furthermore, in case of p-xylene, the white crystals IIc, $C_{16}H_{16}$, m.p. 43-44° (25% yield) and acetate IIIa (15% yield), were obtained. This compound IIc was identical in all respects with authentic trans-2,5-dimethyl stilbene (IIc; $R_1=R_2=CH_3$, $R_3=H$) which was prepared from p-xylidine and trans-cinnamic acid.(7) However, in case of mesitylene, no stilbene derivative was obtained. This can be attributed to steric hindrance of three methyl groups on benzene.

When a solution of complex I in benzene was heated at reflux in the absence of acetic acid, styrene was recovered quantitatively, and no stilbene was obtained. Similarly, no stilbene was obtained, complex I being treated with benzene in the presence of dry hydrogen chloride in place of acetic acid. On the other hand, in case of monochloroacetic acid, stilbene IIa (18% yield) and phenyl methyl carbinol monochloroacetate (IIIb; $R_4=CH_2Cl$, 7% yield) which was identical with an authentic sample, were obtained.

These results indicate that carboxylic acid plays an important role on this reaction. Thus, it is clear that the reaction of styrene complex I with aromatic compounds gives aromatic substituted olefin products through a direct substitution in the presence of carboxylic acid, and that phenyl methyl carbinol acetates are formed as byproducts by the addition of carboxylic acid to styrene.

Moreover, it was found that styrene could be produced by the direct substitution of benzene with ethylene. Details will be reported in the near future.

The scope, and the mechanism of the reported useful reaction, and the relation between the yield of stilbene derivatives and the basicity of aromatic compounds, are now under investigation.

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