Synthesis through Oxypalladation. The Reaction of Acetylacetone with Styrene in the Presence of Palladous Chloride

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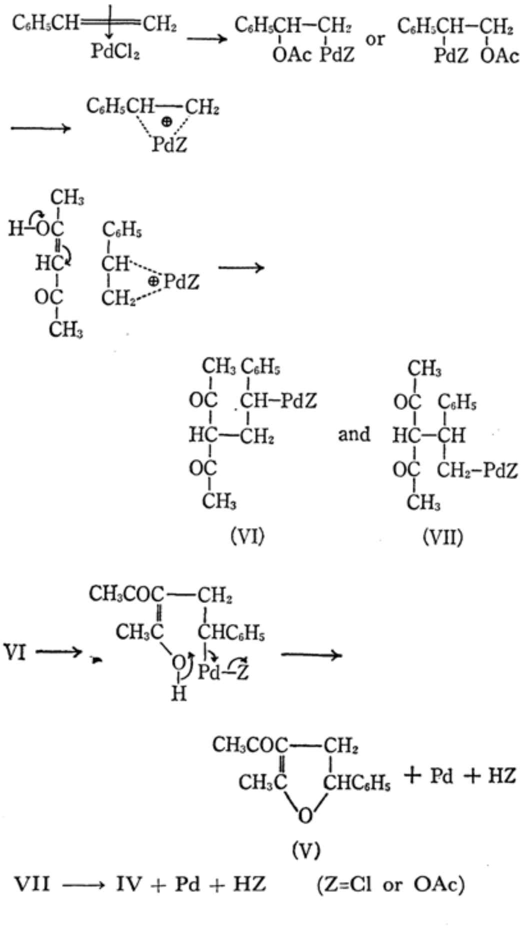
The reactions of olefin-palladium complexes are of current interests. In particular, the problem whether the reactions are those of π-complexes themselves or proceed through oxypalladates is the key point to elucidate the mechanism of these reactions, since it was found recently that oxypalladation of olefins takes place with palladous salt under certain conditions.[1] In previous papers,[2-4] it has been demonstrated that the active methylene of acetylacetone can be alkylated with oxymercurial, oxythallate and oxyplumbate of styrene to form acetylacetones which are substituted with metallo-phenethyl groups. These intermediate organometallics react further to form several final products, depending on the kinds of the metals and the conditions. In this communication, it is reported that the reaction of acetylacetone with styrene in the presence of palladous chloride gives the products which are similar to those obtained by the same reaction with oxythallate and oxyplumbate, and that the reaction proceeds through oxypalladation presumably.

A mixture containing 300 m*l* of acetic acid, 1 g of palladous chloride, 50 g of cupric chloride (hydrated) and 20 g of styrene was heated at 75°C for 18 hr. The reaction mixture was greenish grey and contained solid copper chelate of acetylacetone. After cooling to 55—60°C, 20 g of 70% perchloric acid was added. The color of the mixture turened to brown, although no heat evolution was observed. After standing at room temperature for 5 hr under stirring, the mixture was filtered to remove precipitates. The filtrate was added with 900 m*l* of water, extracted with benzene. The benzene extract was washed with aqueous sodium bicarbonate and then with water and distilled under reduced pressure. The following fractions were obtained: Fraction 1, bp 35—47°C/28 mmHg, 10 g (recovered styrene); fraction 2, bp 60—110°C/8 mmHg, 3.7 g (α-acetoxyethylbenzene (I) and styrene dichloride (II) in a ratio of 95 : 5); fraction 3, bp 122—146°C/3 mmHg, 3.05 g; residue 2 g. Gas chromatographic analysis showed that fraction 3 contained α, β-diacetoxyethylbenzene (III, 0.5 g), unidentified product (0.4 g), 3-acetoxy-2-methyl-4-phenyl-4, 5-dihydrofuran (IV, 0.5 g), 3-acetyl-2-methyl-5-phenyl-4, 5-dihydrofuran (V, 0.85 g) and styrene dimer (0.8 g). Infrared spectrum of fraction 3 showed distinct bands at 1670 $\nu_{C=O}$) and 1600 cm^{-1} ($\nu_{C=C}$) which are characteristic for the dihydrofuran.

Since dihydrofurans IV and V were obtained by the reactions of acetylacetone with oxythallate and oxyplumbate under similar conditions, it is natural to assume that the present result of the formation of the same products IV and V can be explained by the same mechanism. It is most likely that π-complex of styrene-palladous chloride (formed at first) is converted to oxypalladate and reacts with acetylacetone by the following sequence:



VII ⟶ IV + Pd + HZ (Z=Cl or OAc)

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