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REACTION OF ORTHO-PALLADATED DIMETHYLBENZYLAMINE WITH STYRENE: UNEXPECTED SALT EFFECT

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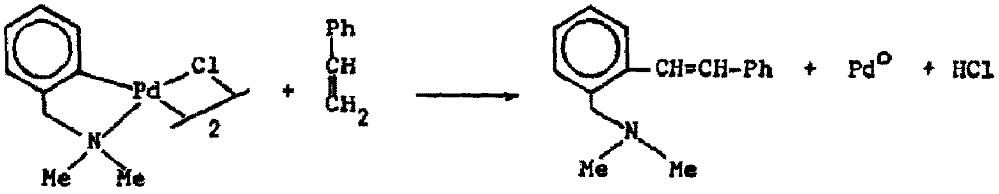
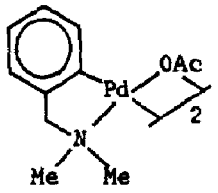
Summary: Treatment of ortho-palladated complex I with styrene in benzene - acetic acid mixture gives complex IV. The reaction is strongly accelerated in the presence of $NaClO_4$ or $LiClO_4$.

In the recent years the reactions of ortho-palladated aromatic molecules with olefins have been intensively studied. Tsuji was the first to report that di-μ-chloro-bis(N,N-dimethylbenzylamine-2-C,N)dipalladium(II) (I) reacted with styrene in acetic acid at room temperature to give the stilbene derivative II[I]



I II

Any additional information was, however, absent in the reference[I]. Later the reaction of ethyl acrylate with palladated I-dimethylaminomethylnaphtalene was reported[2]. Interaction of complex I with enones, proceeding in benzene or toluene in the presence of NEt_3, was studied by Holton more thoroughly[3]. Vinylation of cyclopalladated acetanilides was reported to proceed under the same conditions[4]. There are several examples of reactions of olefins with pseudo-aromatic ortho-palladated compounds[5]. Very recently Heck and coworkers reported reactions of acetato analog of I with several olefins[6]. They have shown, in particular, that complex III reacts with methyl acrylate at I50° C for 48 h giving I7,5% yield of trans-methyl-o-dimethylaminomethylcinnamate. However, no products have been isolated in the case of styrene or ethylene.



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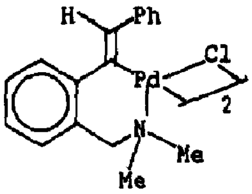

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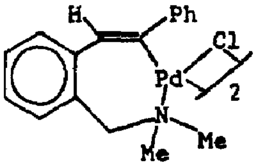


V

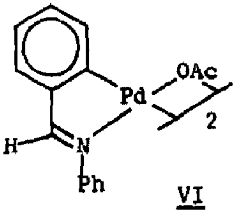
Recently we began to study reactions of complex I with styrenes and our first results differ significantly from those in references^{I,6}. Our findings show that under appropriate conditions complex I reacts with styrene to form not II but its palladated derivative IV.

Results and Discussion

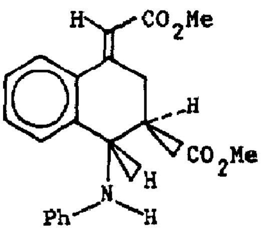
We have found that treatment of complex I with styrene in benzene or toluene in the presence of triethylamine in the temperature range 70-II0° C gives neither II nor any other product. This is in agreement with the Heck's observation^{6} that complex III does not react smoothly with styrene in acetonitrile even at I50° C.

Much more satisfactory results were obtained using benzene - acetic acid (I:I) mixture as a solvent. Holton showed that addition of enones to I is accelerated in the presence of acetic acid^{3}. We have found that HOAc also promotes the reaction with styrene. Interaction between I and styrene is completed at 50° C within 30 h. Purification of the crude product by column chromatography gives pale yellow-green complex IV in a I8% yield. Structure IV was established on the basis of analitical data, UV, IR, and ^{I}H NMR spectroscopy (see Experimental) and confirmed by its protonolysis with hydrochloric acid. Addition of HCl to dioxane solution of IV turns the pale yellow-green colour of solution to dark-red indicating decomposition of IV and formation of $PdCl_4^{2-}$ ion. Treatment the resulting solution with an anion exchange resin gives palladium-free solution of II. The latter was concentrated, and light-brown crystalls of II were obtained, identified as II·HCl·H_2O.

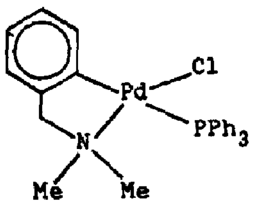
The results obtained do not, of course, indicate the exact coordination mode of palladium(II) in reaction product. Thus, several isomers of IV, e. g. V, are possible. We prefer structure IV since it is strongly supported by Heck's results on reaction of complex VI with two molecules of methyl acrylate giving VII.



VI



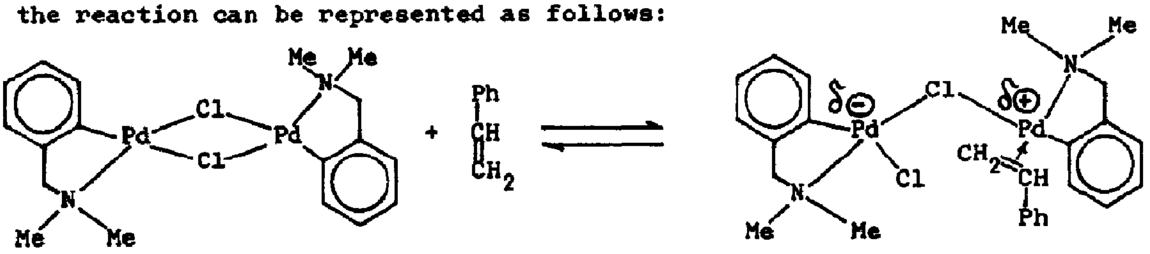
VII



VIII

Unexpectedly we have found that reaction between I and styrene is strongly accelerated in the presence of electrolytes. For instance, the reaction time can be shortened (and the yield of IV slightly raised) from 30 to I h in the presence of 0.I M sodium perchlorate. Lithium perchlorate, but not sodium acetate, can be used instead of $NaClO_4$, because NaOAc promotes the formation of trans,trans-I,4-diphenyl-I,3-butadiene. In general, this strong salt effect in formation of IV is consistent with the rate acceleration by HOAc which is more polar solvent than benzene or toluene.

Positive salt effect reveals a formation of rather polar transition states or intermediates. This is consistent with the assumption that the initial step of the reaction can be represented as follows:



IX

Further transformations of IX can involve addition of the Pd-C group to the double bond followed by elimination of palladium hydride and formation of coordinated II. Apparently, binuclear structure of IX favoured the transfer of hydride on the neighbouring palladium atom not coordinated with olefin. This leads to reduction of the second palladium ion and formation of the metallated complex IV. Preliminary experiments with monomeric adduct VIII showed that the monomeric complex was much less reactive than I in the reaction with styrene. This result is indicative of the significance of dimeric species in the reaction studied. However, it is noteworthy that in the case of enones, which are much more reactive than styrene, splitting of chloro bridges in I with PPh_3 to give VIII, does not lead to the marked rate retardation^3.

Experimental

Complex I was prepared as followed. N,N-dimethylbenzylamine (0.87 g, 6.45 mmol) was added to the solution of Li_2PdCl_4 (I.69 g, 6.45 mmol) and NaOAc (0.54 g, 6.45 mmol) in aqueous 80% dioxane. The solution was allowed to stand at room temperature for 24 h. The yellow precipitate was filtered, washed with water-dioxane mixture, and dried in vacuo over P_2O_5. Yield 70%. UV (benzene): $\lambda(max)$ = 343 nm, ε =2080 $M^{-I}cm^{-I}$; lit.^{7} λ(max)=340 nm, ε = 2520 $M^{-I}cm^{-I}$.

Reaction of complex I with styrene. The solution of styrene (0.I75 ml, I.53 mmol) in I5 ml of HOAc was added to the solution of I (0.405 g, 0.74 mmol) in I5 ml of benzene. The reaction mixture was thermostated at 50° C for 30 h in the absence or I-2 h in the presence of 0.2 M $NaClO_4$ or $LiClO_4$ in initial HOAc. The reaction mixture was filtered to remove the precipitated palladium, and the filtrate was evaporated in vacuo. The residue was dissolved in $CHCl_3$, washed with water, dried over $MgSO_4$, and column chromatographed on silica gel ($CHCl_3$). The first pale-yellow band was separated, concentrated, and complex IV was precipitated by addition of heptane. Yield I8% in the absence and 24% in the presence of $NaClO_4$ (based on I, theorethical yield 50%). UV spectrum of IV (EtC shows the typical stilbene-like pattern indicative of the existance of conjugation between double C=C bond and two phenyl groups: λ (max)=297 nm, ε=37700 M^{-1} cm^{-I}; IR (KBr) I6I0, I585,and I560 cm^{-I} (C=C); 975 cm^{-I} (trans-H-C=CPd); ^{I}H NMF ($CDCl_3$, δ) 6.80- 7.45 (m, 9 aromatic protons and I vinylic proton), 4.I6 (s, 2 methylene protons), and 2.90 (s, 6 methyl protons); m. p. I5I-I56° C (dec.). Molecular weight (ebullioscopic in $CHCl_3$) 748, calcd. 756 (dimer). Anal.: Found C, 52.90; H, 4.80; N, 3.5I; Cl, 9,40; Pd, 28.05; Calcd. for $C_{I7}H_{I8}NPdCl$: C, 53.96; H, 4.76; N, 3.70; Cl, 9.38; Pd, 28.07%.

Reaction of complex IV with HCl. Complex IV (0.035 g, 0.046 mmol) was dissolved in a minimum quantity of dioxane and 0.5 ml concentrated HCl was added. The solution was diluted with water and brought to column with an anion exchange resin (IRA-400, Cl^- form). The resulting solution was concentrated on water bath and allowed to stand overnight at room temperature. The crystalls formed were filtered and washed with water. UV spectrum of II$\cdot HCl\cdot H_2O$ (EtOH): λ(max)=295 nm, ε=23700 $M^{-I}cm^{-I}$; IR (KBr)2720 (R_3NH^+); I600 (C=C), and 980 cm^{-I} (trans-H-C=C-H). Anal.: Found: C, 70.0; H, 8.3; Cl, I2.2; Calcd. for $C_{I7}H_{22}NClO$ C, 70.0; H, 7.5; Cl, I2.8%.

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