Aromatic Substitution of Olefins. Reaction of [$^2H_2$]Styrene with Benzene in the Presence of Palladium(II) Acetate[1]

By S. DANNO

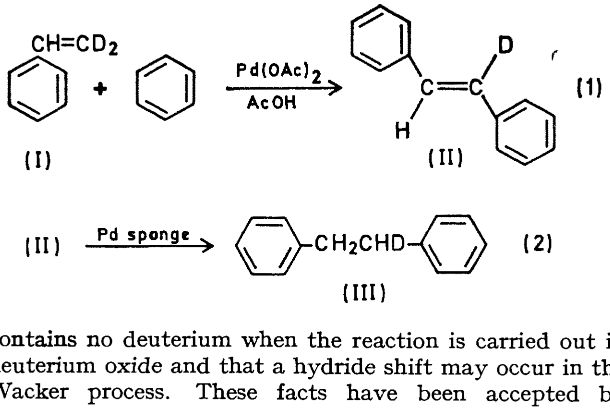
(*Polymer Research Laboratory, Ube Industries Ltd., Ichihara, Chiba, Japan*)

and I. MORITANI* and Y. FUJIWARA

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

Summary No hydride shift occurs in the course of the reaction of [$\beta\beta$-$^2H_2$]styrene with benzene catalysed by palladium(II) acetate.

SMIDT *et al.*[2] have reported that in the oxidation of ethylene with palladium salts, the acetaldehyde produced contains no deuterium when the reaction is carried out in deuterium oxide and that a hydride shift may occur in the Wacker process. These facts have been accepted by Henry[3] and Moiseev *et al.*[4]



Then we were interested in whether the hydride shift also occurs in the previously reported reaction of olefins with aromatics.[5] In order to study this point, the reaction of [$\beta\beta$-$^2H_2$]styrene (I)[6] was performed in a solution of dry acetic acid and benzene for 8 hr. (reaction 1). The monodeuteriostilbene formed was hydrogenated on palladium sponge (reaction 2), because the chemical shift of the olefinic proton in the compound (II) is too similar to that of the aromatic protons for one to be able to calculate the ratio of their integrated areas in the 100 MHz spectrum. The results are summarized in the Table.

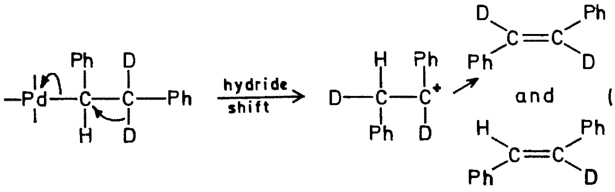
The reactions of [$\beta\beta$-$^2H_2$]*styrene with benzene*

Reactant	D-content of stilbene[b]	Chemical shifts for compound (III)
$PhCH{=}CD_2$[a]	99 ± 2·9	methylenic proton, 7·14 (s) phenylic protons, 2·9 (m)
$\frac{PhCH{=}CD_2{}^a}{PhCH{=}CH_2} = 1{\cdot}00$	50 ± 0·3	methylenic proton, 7·14 (s) phenylic protons, 2·9 (m)

[a] The 100 MHz spectrum showed this to be 102—104% deuteriated.

[b] Calculated on the basis that D-content of stilbene containing one olefinic deuterium is 100%.

If a hydride shift occurs in the reaction, the D-content of stilbene would be 150% (Table). However the D-content found was 99 ± 2·9%. And in the case of [$^2H_2$]-styrene/styrene = 1·00, the D-content was 50 ± 0·3%. This result suggests that no hydride shift occurs in the reaction. The reaction of *p*-methoxy[$\beta\beta$-$^2H_2$]styrene with benzene gave analogous results. Thus it is reasonable to assume the existence of a σ-bonded intermediate in the aromatic substitution of olefins[7] and that the reaction proceeds through a different mechanism from that of the Wacker process.



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