NOTES

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Aromatic Substitution of Olefins. XXII. Unusual Reaction of *p*-Bromostyrene with Benzene in the Presence of Palladium(II) Acetate[1]

Hidetsugu TANAKA, Yuzo FUJIWARA, Ichiro MORITANI, and Shiichiro TERANISHI
Department of Chemistry, Faculty of Engineering Science, Osaka University, Machikaneyama, Toyonaka, Osaka 560

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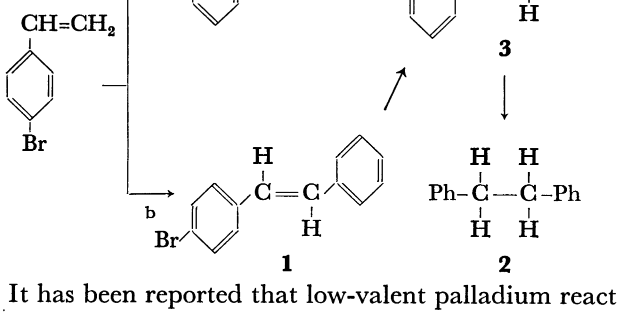
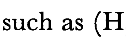
Synopsis. The reaction of *p*-bromostyrene with benzene in the presence of palladium(II) acetate gave unexpected bibenzyl (**2**) and *trans*-stilbene (**3**) in 12% and 5% yields respectively, in addition to the usual substitution product (**1**, 47%). This result shows that dehalogenation and subsequent hydrogenation accompany the aromatic substitution of olefins when both iodides and bromides are used.

We have reported a novel reaction of olefins with aromatic compounds to produce aromatic-substituted olefins *via* direct substitution in the presence of palladium (II) salts.[2]

In the course of our study on the aromatic substitution of olefins, we have performed the reaction of *p*-bromostyrene with benzene in the presence of Pd(OAc)$_2$ in the hope of obtaining *p*-bromo-*trans*-stilbene as the sole product. However, from this reaction, we obtained bibenzyl (**2**) and *trans*-stilbene (**3**) in yields of 12% and 5% respectively with a 47% yield of the usual substitution product, *p*-bromo-*trans*-stilbene (**1**).[3] This suggested that the bromine atom of bromostyrene was replaced with hydrogen by the action of Pd(OAc)$_2$. To chek this point, the dehalogenation and hydrogenation of halobenzenes with Pd(OAc)$_2$ were examined. Refluxing of bromobenzene with Pd(OAc)$_2$ gave the hydrogenolysis product (benzene) in 16% yield and, from iodobenzene, a 55% yield of benzene was obtained.[4]

These results show that Pd(OAc)$_2$ causes the dehalogenation-hydrogenation reaction and that the reactivity of halobenzenes is I>Br≫Cl. Thus it would be possible to describe two paths (a and b) for formation of **3**: one is the route *via* styrene which is derived from a debromination-hydrogenation of *p*-bromostyrene, and the other is the route involving a debromination-hydrogenation of **1**, which is the usual aromatic substitution product.[5] Compound **2** is formed *via* hydrogenation of **3**.[5] The reaction paths are shown in the following Scheme:



It has been reported that low-valent palladium reacts with halides (RX) to form organopalladium σ-complexes (R–Pd–X) *in situ*.[6] In the present case, an aryl-palladium σ-complex such as (H$_2$C=CH--PdBr) would also be formed, *via* the oxidative addition of Pd, but it would be decomposed by hydrogen to give hydrogenolysis products[5] without any further reaction with the olefins.

The results described here call for attention when halides, especially iodides and bromides, are employed in the aromatic substitution of olefins by palladium (II) salts.

Experimental

p-Bromostyrene was prepared from dehydration of 1-(*p*-bromophenyl)ethanol, bp$_{16}$ 88—89 °C.

Reaction of p-*Bromostyrene with Benzene.* A solution of Pd(OAc)$_2$ (4.6 mmol), and *p*-bromostyrene (4.6 mmol) in a mixture of benzene (50 ml) and acetic acid (10 ml) was heated at 80 °C with stirring for 8 hr. The resulting mixture was worked up as described already.[7] The products were separated by preparative glc to give **1**, **2**, and **3**, which were all assigned by a comparison with authentic samples, mp of **1**, 138—139 °C (EtOH) (lit,[8] mp 139 °C).

Dehalogenation-hydrogenation of Aryl Halides. A solution of Pd(OAc)$_2$ (4.6 mmol) and bromobenzene (50 ml) was refluxed for 8 hr using octane as an internal standard. After work-up, glc analysis showed a 16% yield of benzene. Similarly, iodobenzene was refluxed using nonane as an internal standard to give a 55% yield of benzene. Under similar reaction conditions, chlorobenzene did not result in any formation of benzene.

References

1) Taken in part from the M. S. Thesis of H. Tanaka, Osaka University, 1971; Part XXI: M. Watanabe, M. Yamamura, I. Moritani, Y. Fujiwara, and S. Teranishi, This Bulletin, **47**, 1035 (1974).

2) For a review see I. Moritani and Y. Fujiwara, *Synthesis*, **1973**, 524.

3) Yields are all based on palladium acetate used.

4) Hydrogen would be derived mainly from the saturated hydrocarbons used as internal standards.

5) Hydrogen evolved from the usual aromatic substitution reaction would be used for the debromination-hydrogenation.

6) For example see P. Fitton and E. A. Rick, *J. Organometal. Chem.*, **28**, 287 (1971); K. Mori, T. Mizoroki, and A. Ozaki, This Bulletin, **46**, 1505 (1973); A. Schoenberg, I. Bartoletti, and R. F. Heck, *J. Org. Chem.*, **39**, 3318 (1974).

7) Y. Fujiwara, I. Moritani, R. Asano, and S. Teranishi, *J. Amer. Chem. Soc.*, **91**, 7166 (1969).

8) F. Bergman, J. Weizman, and D. Schapiro, *J. Org. Chem.*, **9**, 408 (1944).