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# Aromatic Substitution of Olefins XV. The Steric Course of the Reaction

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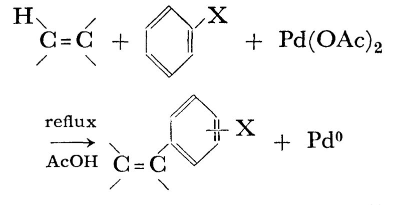
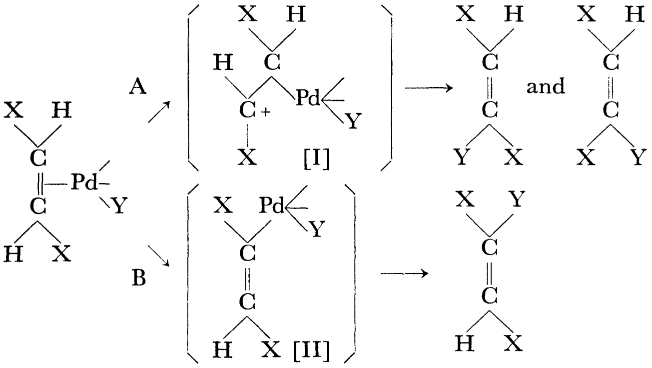
In previous papers, we have reported that aromatic compounds react smoothly with olefins in the presence of palladium acetate to produce aryl-substituted olefins (Eq. (1))[1] and that the reaction proceeds through a different mechanism from that of the Wacker process,[2] for no hydride shift occurs in the course of the aromatic substitution reaction of olefins.



(1)

It has been reported that, in the Wacker process,[3] a $\sigma$-complex (I) may be formed after the nucleophilic attack of an anion on the olefin-Pd $\pi$-complex, followed by the $\pi$-electron transfer:



In the aromatic substitution of olefins, we have proposed a mechanism in which an olefin-palladium $\sigma$-complex (II) is formed through hydrogen abstraction from the olefin.[4]

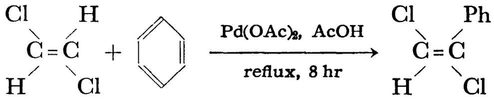
If the aromatic substitution reaction proceeds *via* an intermediate (I) according to the path A, a free rotation about the C–C axis becomes possible, for the electronic configuration changes from $sp^2$ to $sp^3$ hybridization, and the products will be a mixture of *cis*- and *trans*-isomer.

Contrary to this, in the case of the path B, olefinic carbon atoms will remain in the intermediate (II), so the reaction will proceed with a retention of the configuration.

Thus, it is possible to determine the reaction path if the olefins which do not isomerize under the reaction conditions are allowed to react with benzene, and the stereochemistry of the product can be investigated.

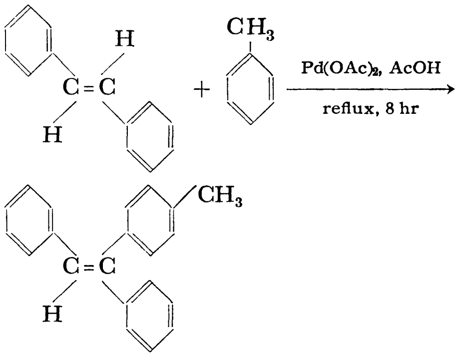
Therefore, *trans*-stilbene, *cis*- and *trans*-dichloroethylenes were selected as olefins, for they do not isomerize in the course of the reaction.

The reaction of *trans*-dichloroethylene with benzene proceeded in acetic acid in the presence of palladium acetate. Phenyl-*trans*-dichloroethylene was obtained in a 42% yield (based on pallaium), but no phenyl-*cis*-dichloroethylene was detected (Eq. (2)). Similary, *cis*-dichloroethylene reacted with benzene and produced phenyl-*cis*-dichloroethylene.



(2)

Moreover, the *trans*-stilbene was reacted with benzene to produce *p*-tolyl-*trans*-stilbene. The reaction of *cis*-stilbene with toluene was not the same, however, because it is isomerized to the *trans*-isomer when treated under the same conditions for two hours.



(3)

These results strongly demonstrate that the substitution reaction proceeds with a retention of the configuration of the olefins, and the path B is favored for the aromatic substitution reaction of olefins. Moreover, it is reasonable to assume the existence of an olefin-palladium $\sigma$-bonded intermediate in the reaction.

## Experimental

All the boiling points are uncorrected. The infrared spectra recorded by means of a Hitachi EPI-S2 IR spectrophotometer, while the ultraviolet spectra were obtained on a Hitachi-EPS-2U spectrophotometer. The NMR spectra were obtained by the use of a Japan Electron Optics JNM-4H-100 or JNM-C-60HL spectrometer, using tetramethylsilane as the internal standard. Chemical shifts are given on the $\tau$-scale, together

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1) For example, Y. Fukiwara, I. Moritani, S. Danno, R. Asano, and S. Teranishi, *J. Amer. Chem. Soc.*, **91**, 7166 (1969).

2) S. Danno, I. Moritani, and Y. Fujiwara, *Chem. Commun.*, **1970**, 610; S. Danno, I. Moritani, Y. Fujiwara, and S. Teranishi, *J. Chem. Soc., B*, in press.

3) J. Smidt, W. Hafner, R. Jira, R. Sieber, and J. Sedlmeier, *Angew. Chem. Internat. Edn.*, **1**, 80 (1962); P. M. Henry, *J. Amer. Chem. Soc.*, **86**, 3242 (1964); *ibid.*, **88**, 1596 (1966); I. I. Moiseev, M. N. Vargaftik, and Ya. K. Syrkin, *Dokl. Akad. Nauk SSSR*, **153**, 140 (1963).

4) S. Danno, I. Moritani, and Y. Fujiwara, *Tetrahedron*, **25**, 4819 (1969).

with the splitting patterns and the relative integrated area.

*General Procedure for the Reaction.* A mixture of the palladium acetate, an equivalent amount of the olefin, acetic acid, and the aromatic compound was stirred for 8 hr at reflux. The reactions were carried out with an excess of the aromatic compound, which behaved as both a reactant and a solvent. The resulting mixture was filtered to remove the palladium metal, and then the filtrate was poured into water and the organic layer was separated. The organic layer was treated with an aqueous sodium bicarbonate solution, washed with water to free it from acetic acid, and then dried over anhydrous magnesium sulfate. After the evaporation of the solvent, the products were isolated by gas chromatography. Analyses of the products were carried out by the use of a Yanagimoto GCG-3 gas chromatograph, using an Apiezon L, Carbowax 20M, or SE-30 column. Identities with the products formed were proved by IR, UV, or NMR comparison with authentic samples.

*Reaction of* trans-*Stilbene with Toluene.* In a solution of dry toluene (300 m*l*) and dry acetic acid (100 m*l*), we dissolved palladium acetate (28.8 mmol, 6.47 g) and *trans*-stilbene (28.8 mmol, 5.25 g). The mixture was then refluxed for 8 hr. The resulting mixture was filtered to remove the reduced palladium metal and the filtrate was poured into water. The organic layer was treated with an aqueous sodium bicarbonate solution, washed with water, and then dried over $MgSO_4$. After the evaporation of the solvent, the products were separated by vpc to give 1.79 g of *p*-tolyl-*trans*-stilbene; UV spectrum: $\lambda_{max}^{EtOH}=312\ m\mu$ ($\varepsilon$: $2.08\times10^4$); NMR spectrum (in $CCl_4$): 2.8(m,14H), 3.17(s,1H), and 7.65$\tau$ (s, 3H).

*Preparation and Separation of* p-*Tolyl*-cis *and* trans-*Stilbenes.* *p*-Methylbenzophenone (10 g) dissolved in absolute ether (30 m*l*) was added, drop by drop, to the Grignard reagent prepared from freshly distilled benzyl chloride (8.3 g) and magnesium shoot (1.6 g). After having been refluxed for 1.5 hr, the reaction mixture was hydrolysed with cold water. The residual oil was refluxed for 2 hr with 20% sulfiic acid (70 m*l*) to dehydrate the alcohol thus produced. *p*-Tolylstilbene, (175—182°C/2.5 mmHg[5]) was obtained in a 94% yield. Found: C, 93.10; H, 6.82%. Calcd for $C_{21}H_{18}$: C, 93.29; H, 6.71%.

The *p*-tolyl-*cis* and *trans*-stilbenes prepared by the above described method were separated by VPC (10% SE-30 on Celite 545, 2 m×6 mm, 260°C, 30 m*l* He/min). *p*-Tolyl-*cis*-stilbene; UV spectrum: $\lambda_{max}^{EtOH}=314m\mu$($\varepsilon$: $4.45\times10^4$); NMR spectrum (in $CCl_4$): 2.9(m, 14H), 3.19(s, 1H), and 7.62 $\tau$ (s, 3H). *p*-Tolyl-*trans*-stilbene; the UV and NMR spectra have been described above.

*Preparation of* cis-*Dichlorostyrene.* This compound was prepared by the methods described by Dycherhoff.[6] A mixture of $\omega$-chloroacetophenone (8 g) and phosphorus pentachloride (10.8 g) were heated at 135°C for 2 hr, and the product was distilled in a boiling range of 225—234°C. The distillate was dried over $MgSO_4$ and then redistilled (bp 221—224°C). This product was separated and purified by VPC. NMR Spectrum (in $CCl_4$): 3.0 (m, 5H) and 3.16$\tau$ (s, 1H). Also, *trans*-dichlorostyrene was prepared by the method of Koenig and Wolf.[7] Bp 90—93°C/10 mmHg; IR spectrum (direct): 695, 760 (monosub. benzene), and 1660 cm$^{-1}$; NMR spectrum in $CCl_4$): 2.58 (m, 5H) and 3.33 $\tau$ (s, 1H).

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5) B. Hoei, *Bull. Soc. Chim. Fr.*, **1946**, 117.

6) R. Dycherhoff, *Ber.*, **10**, 120 (1877).

7) J. Koenig and V. Wolf, *Tetrahedron Lett.*, **1970**, 1629.