Tetrahedron. Vol. 25, pp. 4819 to 4823. Pergamon Press 1969. Printed in Great Britain

AROMATIC SUBSTITUTION OF OLEFIN—IX
REACTIONS OF OLEFINS CONTAINING A POLAR GROUP WITH BENZENE[1]

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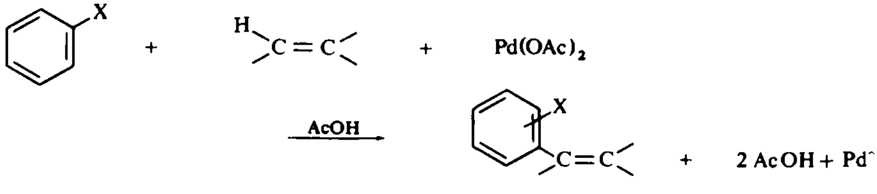
(*Received in Japan* 19 *May* 1969; *Received in the UK for publication* 10 *July* 1969)

Abstract—The phenylation of olefins containing a polar group was carried out in the presence of palladium acetate and acetic acid. The reaction mechanism is discussed.

INTRODUCTION

IN PREVIOUS papers,[2] we reported that the hydrogen of olefins is readily substituted by benzene. Palladium acetate is the most effective catalyst, although the reactivity is influenced by the ligands of palladium(II).



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Although the direction of the substitution is strongly influenced by a substituent on the aromatic compound, this does not affect the reactivity of styrene with monosubstituted benzenes.[3]

In the present paper the substitution reaction of benzene with olefins containing polar groups such as CN, OAc or OEt has been investigated.

RESULTS AND DISCUSSION

Acrylonitrile and vinyl acetate were selected as olefins with an electron attracting group, and ethyl vinyl ether as the olefin with an electron donating group. The experimental results are summarized in Table 1.

The phenylation reactions of these olefins proceeded smoothly, acrylonitrile, yielding *trans*-β-cyanostyrene and its *cis*-isomer in 17% and 8% yields respectively, the total yield (25%) being lower than that of the reaction of styrene with benzene (90%).[2]

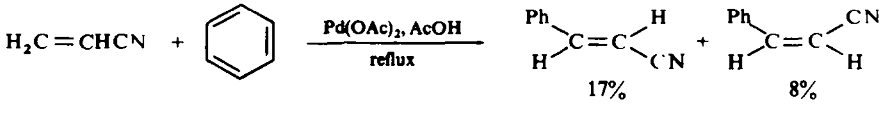

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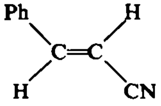
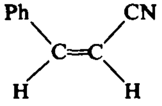
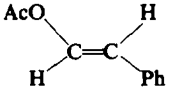
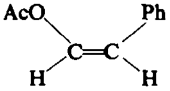
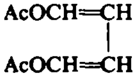
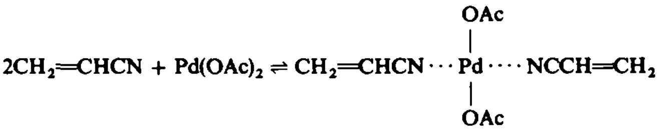
TABLE THE REACTIONS OF BENZENE WITH OLEFINS CONTAINING THE POLAR GROUP BY $Pd(OAc)_2$

Olefin	Products (composition %)			Total yield* (%)
$NCCH{=}CH_2$	 I 68	 II 32		25
$AcOCH{=}CH_2$	 III 28	 IV 16	 $\begin{array}{l}AcOCH{=}CH\\ \qquad\qquad\vert\\ AcOCH{=}CH\end{array}$ V 25	
	$AcOCH{=}C(Ph)C(Ph){=}CHOAc$ VI 31			
$C_2H_5OCH{=}CH_2$	$PhCH{=}CHOC_2H_5$ VII 9	$PhCH{=}C(OAc)OC_2H_5$ VIII 75		13
	$AcOCH{=}CHOC_2H_5$ IX 16			

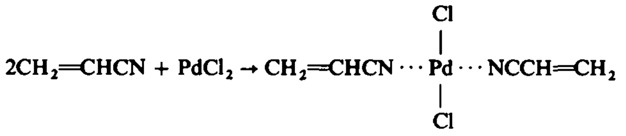
* based on Pd(II).

This low reactivity may be due to the intermediate formation of an acrylonitrile-palladium acetate complex, which is inactive by shielding the reaction site of palladium(II).



$$2CH_2{=}CHCN + Pd(OAc)_2 \rightleftharpoons CH_2{=}CHCN\cdots\overset{\overset{OAc}{|}}{\underset{\underset{OAc}{|}}{Pd}}\cdots NCCH{=}CH_2 \qquad (3)$$

Acrylonitrile reacts easily with $PdCl_2$ to give dichloro-bis(acrylonitrile)palladium(II) complex.[4]



$$2CH_2{=}CHCN + PdCl_2 \rightarrow CH_2{=}CHCN \cdots \underset{\substack{|\\ Cl}}{\overset{\substack{Cl\\ |}}{Pd}} \cdots NCCH{=}CH_2 \qquad (4)$$

In general, since the coordination ability of CN is stronger than that of C═C, the cyanoolefin such as acrylonitrile coordinates to palladium(II) with the lone pair of N, thus hindering the aromatic substitution of olefins.

With vinyl acetate, the phenylation and coupling reaction took place together and dimerization products were also formed in considerable yields.[5]

In contrast, ethyl vinyl ether which has an electron donating group afforded the phenylation products but the yield (13%) was lower than that of the reaction of olefins containing an electron withdrawing group.

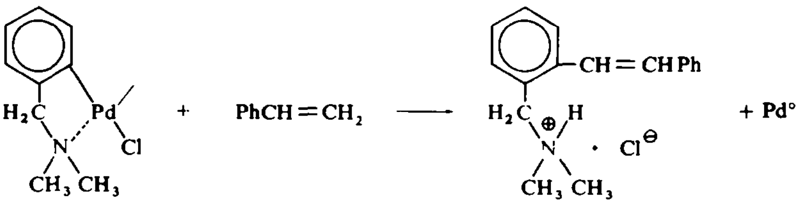
These results show that the reactivity of the olefins decreases in the following sequence:

$$PhCH{=}CH_2 > NCCH{=}CH_2 > AcOCH{=}CH_2 > C_2H_5OCH{=}CH_2.$$

When an electron donating group is replaced by a withdrawing group on the olefinic C atom, the substitution reaction is enhanced, suggesting that the reactivity of the olefins partly depends upon the ease with which the olefin forms a π-complex with Pd(II).

Thus, it becomes clear that the reactivity of various olefins is influenced by the substituent on the olefinic C atom, whereas a substituent of the aromatic compound has no effect on the reactivity, it does affect the direction of substitution.

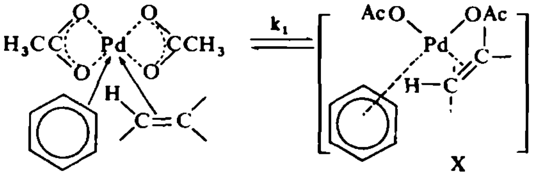
These results suggest that the reaction may proceed through a σ-bonded complex. In fact, Tsuji *et al.* reported that N,N-dimethyl benzylamine-PdCl σ-complex reacts with styrene to give a good yield of N,N-dimethyl-2-styryl-benzylamine hydrochloride.[6]



(5)

Since the σ-bonded benzene derivative can react with styrene in acetic acid to afford the stilbene derivative, the σ-bonded benzene may be an intermediate in the substitution reaction.

The mechanism we propose for this reaction is as follows:[7] Consider the olefin-benzene-palladium system:



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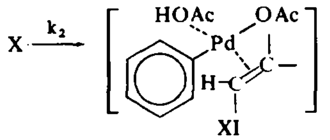

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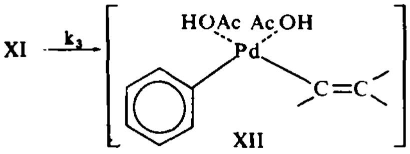

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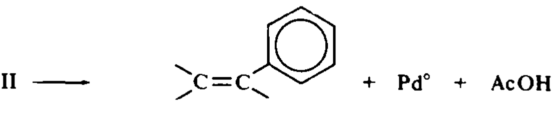

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As Wilkinson *et al.* pointed out,[8] palladium acetate exists in a monomeric form at high temperatures. Benzene and olefin coordinate with the palladium acetate and form a doubly coordinated π-complex (X) which may be transformed to a σ-complex (XI). This is followed by formation of the σ-bond between palladium and olefin. Then the intermediate XII rapidly decomposes into phenylated olefin, metallic palladium and acetic acid.

In these processes, the rate-determining step may be k_3 where a σ-bond develops between palladium and olefin. In this way, we can explain why the substituent of an aromatic compound influences the direction of the substitution but not the reactivity, while the substituent of olefins influences the reactivity.

EXPERIMENTAL

The reactions of acrylonitrile, vinyl acetate, or vinyl ethyl ether were carried out as in the previous paper.[1] The products were identified as follows.

(*a*) *Reaction of acrylonitrile.* Reaction products I and II were separated by VPC. Compound I: IR spectrum (neat): 690 and 750 cm^{-1} (momosub. benzene), 965 cm^{-1} (*trans* CH), 1620 cm^{-1} (C═C), and 2220 cm^{-1} (CN); NMR spectrum (in CCl_4): 2·6 (m, 5) and 4·33 (m, 2); (Found: C, 83·36; H, 5·52; N, 10·69. C_9H_7N requires: C, 83·69; H, 5·46; N, 10·85%). Compound II: IR spectrum (neat): 690, 750, 1615 and 2220 cm^{-1}; (Found: C, 83·80; H, 5·52; N, 10·74. C_9H_7N requires: C, 83·69; H, 5·46; N, 10·85%). The UV spectrum of a mixture of I and II has λ_{max} (in EtOH): 217·5 (ε: 6500), 223 (ε: 5400) and 275 mμ (ε: 9000). Compounds I and II were assigned as *trans*- and *cis*-β-cyanostyrene by comparison of the IR spectra and the retention times with those of authentic samples.[9]

(*b*) *Reaction of vinyl acetate.* Reaction products were III, IV, V and VI. Compound III: IR spectrum (neat): 695, 755, 965, 1210, 1660 and 1770 cm^{-1} (C═O); (Found: C, 74·60; H, 5·10. $C_{10}H_{10}O_2$ requires: C, 74·05; H, 5·66%). Compound IV: IR spectrum (neat): 695, 750, 1215, 1660 and 1770 cm^{-1}; (Found: C, 74·83; H, 5·09. $C_{10}H_{10}O_2$ requires: C, 74·05; H, 5·66%). Compounds III and IV were assigned as *trans*- and *cis*-β-acetoxystyrene by comparison of the IR spectra and retention times with those of authentic samples.[10] Compound V: IR spectrum (neat): 1220, 1600, 1660 and 1765 cm^{-1}; (Found: C, 56·23; H, 5·60. $C_8H_{10}O_4$ requires: C, 56·47; H, 5·92%). Compound VI: IR spectrum (neat): 680, 750, 1215, 1600 and 1760 cm^{-1}; NMR spectrum (in CCl_4): 2·81 (m, 10), 2·98 (q, 2) and 7·87 (s, 6); (Found: C, 74·92; H, 5·26. $C_{20}H_{18}O_4$ requires: C, 74·52; H, 5·63%).

(*c*) *Reaction of ethyl vinyl ether.* Reaction products were VII, VIII and IX. Compound VII was assigned as β-ethoxystyrene by comparison of the IR spectrum and retention time with those of an authentic sample:[11]

IR spectrum (neat): 690, 755, 1090 and 1650 cm^{-1}; (Found: C, 80·76; H, 8·01. $C_{10}H_{12}O$ requires: C, 81·04; H, 8·16%). Compound VIII: IR spectrum: 695, 760, 1200, 1600 and 1750 cm^{-1}; (Found: C, 69·56; H, 6·72. $C_{12}H_{14}O_3$ requires: C, 69·88; H, 6·86%). Compound IX: IR spectrum (neat): 1105, 1170, 1630 and 1730 cm^{-1}; (Found: C, 55·09; H, 7·27. $C_6H_{10}O_3$ requires: C, 55·37; H, 7·75%).

REFERENCES

[1] Part VII of this series, S. Danno, I. Moritani and Y. Fujiwara, *Tetrahedron* **25**, 4809 (1969).

[2] Part VI of this series, Y. Fujiwara, I. Moritani, S. Danno and R. Asano, *J. Am. Chem. Soc.* in press.

[3] Part VIII of this series, Y. Fujiwara, R. Asano, H. Tanaka and S. Teranishi, *Tetrahedron* **25**, 4815 (1969).

[4] G. N. Shrauzer, *J. Am. Chem. Soc.* **81**, 5310 (1959).

[5] [a] R. Hüttel, J. Katzer and M. Bechiter, *Chem. Ber.* **94**, 766 (1961); [b] C. F. Kohll, R. van Helden, *Rec. Trav. Chim.* **86**, 193 (1967).

[6] H. Takahashi, K. Ohno and J. Tsuji, *The 22nd Annual Meeting of Chem. Soc. Japan* Tokyo, April 3 (1969).

[7] Presented at *The Discussion Meeting of Oil Chemistry of Chem. Soc. Japan* Tokyo, Oct. 5 (1968).

[8] T. A. Stephenson, S. M. Morehouse, A. P. Powell, J. P. Heffer and G. Wilkinson, *J. Chem. Soc.* 3632 (1965).

[9] G. Kruss, *Dtsch. Chem. Ber.* **17**, 1768 (1889).

[10] F. W. Semmler, *Ibid.* **42**, 584 (1909).

[11] J. V. Nef, *Liebigs Ann.* **308**, 270 (1899).