AROMATIC SUBSTITUTION OF OLEFIN—VII REACTIONS OF LOWER OLEFINS WITH BENZENE BY PALLADIUM ACETATE¹

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Abstract—The phenylation of propylene, 1-butene, *trans*- and *cis*-butenes, and 1,3-butadiene with benzene was carried out in the presence of palladium acetate and acetic acid. It was concluded that, although the usual olefins predominantly undergo phenylation, an olefin which can easily form a π -allyl complex gives acetates as major products under the present reaction conditions.

INTRODUCTION

WE HAVE previously reported a novel aromatic substitution of olefins by palladium salts in which the substitution takes place at the double bond of the olefin, giving arylated olefins.

In this reaction, it seems that the substitution proceeds through the activation of both olefin and aromatic compound by coordination to Pd(II), which is then reduced to metallic palladium.

The present paper reports the reactions of propylene, 1-butene, *trans*- and *cis*butenes, and 1,3-butadiene with benzene in the presence of palladium acetate and acetic acid.



RESULTS AND DISCUSSION

In all these reactions, the gaseous olefin was passed through a homogeneous solution of palladium acetate in a mixture of benzene (large excess) and acetic acid. Phenylated products together with reduced metallic palladium, and a small amount of acetates were obtained.

The experimental results are given in Table 1.

In the case of *cis*-butene, the major product is 2-phenyl-*cis*-butene with retention of configuration, whereas 2-phenyl-*cis*-butene is produced with inversion of configuration in the reaction of *trans*-butene with benzene.

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TABLE 1. THE REACTION OF LOWER OLEFINS WITH BENZENE



* based on Pd(II).



In the latter case, 2-phenyl-*trans*-butene may be formed first which then rapidly isomerizes to the *cis*-isomer. In fact, when 2-phenyl-*trans*-butene was treated under similar conditions, it isomerized to the *cis*-isomer almost quantitatively.



Similarly, 2-phenyl-1-butene which was formed in the reactions of both *cis*- and *trans*-butene, may be derived by isomerization of 2-phenyl-*cis*-butene under the reaction conditions.

$$CH_{3} \xrightarrow{CH_{3}} C=C \xrightarrow{Pd(OAc)_{2}, AcOH} CH_{3} \xrightarrow{CH_{2}} CH_{2}$$

$$H \xrightarrow{Ph} CH_{4} \xrightarrow{CH_{2}} CH_{2} \xrightarrow{CH_{$$

Isomerization of 2-phenyl-cis-butene under similar conditions resulted in 20% isomerization to 2-phenyl-1-butene. It is, however, possible that 2-butene first isomerizes and then aromatic substitution occurs at C-2 of 1-butene. The latter process

may be eliminated since in the reaction of 1-butene with benzene the ph group is added exclusively to the less substituted C atom of the double bond due to the steric hind-rance of substituents,¹ and no 2-phenyl-1-butene derivative is produced.

The reactivity of simple lower olefins decreases in the following order; propylene > trans-butene, cis-butene > 1-butene. A comparison of the reactivity of these olefins and styrene is difficult because of the different concentrations of the reacting olefins.

The reaction products of 1,3-butadiene with benzene are complex since phenylation, acetoxylation and coupling take place together although the acetoxylation is predominant.

$$\begin{array}{c} HC \xrightarrow{CH_2} \\ \xrightarrow{CH} \\ \xrightarrow{CH} \\ CH, \end{array} + Pd(OAc)_2 \longrightarrow \begin{bmatrix} CH_2 \\ \xrightarrow{CH} \\ CH \\ CH_2 \\ C$$

This result suggests that the reaction of Eq. (5) occurs easily, giving a π -allyl-palladium complex, and then, the intermediate complex with acetate anion preferentially to give acetates.

To clarify this point, μ -dichloro-bis(π -1-acetoxymethylallyl) palladium(II) was treated with acetic acid and benzene under the reaction conditions. 1-Acetoxy-1,3-butadiene and 1,4-diacetoxy-2-butene were obtained in 19% and 7% yields respectively. Moreover, when silver acetate was added to displace the Cl⁻ ligand with an AcO⁻, the yield of these acetates increased to 20% and 26% respectively. Similarly, in the case of propylene, the reaction proceeds *via* a similar reaction intermediate with respect to the formation of acetoxylated products.

Therefore, it can be concluded that an olefin, which easily forms an π -allyl complex such as butadiene or propylene, gives acetates as major products, while the usual olefins undergo the phenylation under the reaction conditions.

EXPERIMENTAL

Benzene was heated under reflux with Na and distilled. AcOH was dried over P_2O_3 and distilled. IR spectra were recorded with a Hitachi-S2 spectrophotometer; UV spectra were obtained by a Hitachi-EPS-2U spectrophotometer; NMR spectra were recorded by a Japan Electron Optics JNR-4H-100 or JNM-MH-60 spectrometer. Chemical shifts are given in τ -scale together with splitting patterns and relative integrated area. VPC analyses were made by a Yanagimoto GCG-3 gas chromatograph.

General procedure for the phenylation of lower olefins. In a soln of dry benzene (300 ml) and AcOH (100 ml), 6·47 g (28.8 mmole) palladium acetate was dissolved and the olefin gases were bubbled through at a constant rate of 30 ml/min until saturation. The mixture was gently heated under reflux at $\sim 80^{\circ}$ with continued stirring and bubbling for 8 hr. After separation of the precipitated Pd, the mixture was poured into water. The organic layer was separated, the aqueous layer extracted twice with benzene and the combined extracts washed and dried over MgSO₄. Most of the solvent was evaporated under atmospheric press. The residual oil was distilled under reduced press, and the distillate was separated and purified by VPC. The products were identified by comparison of IR spectra and retention time with authentic samples.

(a) Reaction of trans-2-butene. Reaction products were separated and purified by VPC. 2-Phenyl-cisbutene (I) was identified by comparison of the IR and NMR spectra with an authentic sample:² IR spectrum (neat): 690, 750 (monosub. benzene), 830 (H-C=C), and 1595 cm⁻¹ (C=C); UV spectrum: $\lambda_{max}^{EIOH} = 210$ and 244 mµ; NMR spectrum (in CCl₄): 2·83 (m,5), 6·25 (m,1), 8·02 (s,3) and (m,3); (Found: C, 90·95; H, 9·16. C₁₀H₁₂ requires: C, 90·85; H, 9·15%). Compound II: IR spectrum (neat): 700, 770 and 1615 cm⁻¹; NMR spectrum (in CCl₄): 2·75 (m,5), 4·80 (s,1), 5·00 (s,1), 7·50 (qu,2), and 8·91 (t,3); (Found: C, 90·79; H, 9·14. C₁₀H₁₂ requires: C, 90·85; H, 9·15%). Compound III: IR spectrum (neat): 1200 (C-O-C), 1625 and 1730 cm⁻¹ (C=O); (Found: C, 63·03; H, 8·65. C₆H₁₀O₂ requires: C, 63·13; H, 8·83%).

(b) The reaction of cis-butene. Reaction products were I, II and IV. Compound IV: IR spectrum (neat): 820, 1220, 1600 and 1740^{-1} : (Found: C, 62.92; H, 8.95. C₆H₁₀O₂ requires: C, 63.13; H, 8.83%).

(c) The reaction of 1-butene. Reaction products were V, VI, VII and VIII. Compound V: IR spectrum (neat): 690, 740, 965 (trans C—H) and 1595 cm⁻¹; NMR spectrum (in CCl₄): 2·85 (m,5), 3·83 (m,2), 7·88 (m,2) and 8·83 (t,3); (Found: C, 90·72; H, 8·92. $C_{10}H_{12}$ requires: C, 90·85; H, 9·15%). Compound VI: IR spectrum (neat): 690, 750 and 1600 cm⁻¹; NMR spectrum (in CCl₄); 2·84 (m,5), 3·80 (m,2), 7·90 (m,2) and 8·85 (t,3); (Found: C, 91·00; H, 9·00. $C_{10}H_{12}$ requires: C, 90·85; H, 9·15%). Compound VII: IR spectrum (neat): 965, 1200, 1600 and 1755 cm⁻¹; (Found: C, 62·90; H, 8·72. $C_6H_{10}O_2$ requires: C, 63·13; H, 8·83%). Compound VIII: IR spectrum (neat): 1210, 1600 and 1750 cm⁻¹.

(d) The reaction of propylene. Reaction products were IX, X, XI and XII. Compound IX: IR spectrum (neat): 690, 745, 1200, 1600 and 1740 cm⁻¹; NMR spectrum (in CCl₄): 2·80 (m,5), 4·20 (s,1), 7·90 (s,3) and 7·96 (s,3); (Found: C, 74·92; H, 6·97. $C_{11}H_{12}O_2$ requires: C, 74·97; H, 6·86%). Compound X: IR spectrum (neat): 700, 750, 880 (C=CH₂), 1200, 1600, 1660 (C=CH₂) and 1750 cm⁻¹; NMR spectrum (in CCl₄): 2·81 (m,5), 5·35 (m,2), 6·52 (s,1) and 7·99 (s,3); (Found: C, 74·88; H, 6·92. $C_{11}H_{12}O_2$ requires: C, 74·97; H, 6·86%). Compound XI: IR spectrum (neat): 870, 1210, 1600 1750 cm⁻¹; (Found: C, 60·07; H, 7·92. $C_{5}H_8O_2$ requires: C, 59·98; H, 8·05%). Compound XII: IR spectrum (neat): 1220, 1595 and 1730 cm⁻¹; (Found: C, 60·81; H, 7·01. $C_{10}H_{14}O_4$ requires: C, 60·59; H, 7·12%).

(e) The reaction of 1,3-butadiene. Reaction products were XIII, XIV, XV and XVI. Compound XIII was identified with 1-phenyl-1,3-butadiene by comparison of IR, UV and NMR spectra³: IR spectrum (neat): 690, 755 and 1605 cm⁻¹; UV spectrum : $\lambda_{max}^{EtoH} = 219 \cdot 5$, 225 $\cdot 8$, 233 $\cdot 5$ and 280 mµ; NMR spectrum (in CCl₄): 280 (m,5), 3 $\cdot 48$ (m,3) and 4 $\cdot 82$ (m,2); (Found: C, 91 $\cdot 83$; H, 7 $\cdot 63$. C₁₀H₁₀ requires: C, 92 $\cdot 26$; H, 7 $\cdot 74\%$). Compound XIV: IR spectrum (neat): 1220 and 1730 cm⁻¹; NMR spectrum (in CCl₄): 4 $\cdot 23$ (m,2), 5 $\cdot 02$ (m,4) and 8 $\cdot 00$ (m,6); (Found: C, 55 $\cdot 33$; H, 7 $\cdot 24$. C₈H₁₂O₄ requires: C, 55 $\cdot 80$; H, 7 $\cdot 03\%$). Compound XV: IR spectrum (neat): 1220, 1640 and 1740 cm⁻¹; NMR spectrum (in CCl₄): 4 $\cdot 6$ (m,3), 5 $\cdot 9$ (m,2) and 8 $\cdot 00$ (m,3); (Found: C, 64 $\cdot 08$; H, 7 $\cdot 23$. C₆H₈O₂ requires: C, 64 $\cdot 27$; H, 7 $\cdot 19\%$). Compound XVI: IR spectrum (neat): 1220, 1640 and 1740 cm⁻¹; (Found: C, 73 $\cdot 43$; H, 7 $\cdot 52$. C₁₀H₁₂O₂ requires: C, 73 $\cdot 14$; H, 19 $\cdot 4\%$).

 μ -Dichloro-bis(π -1-acetoxymethylallyl) palladium(II) was prepared by the method described by Rowe and White⁴: In a soln of AcOH, PdCl₂, NaOAc and CuOAc were dissolved. Butadiene was bubbled through the soln heated under reflux. The resulting ppt was filtered off and extracted with benzene. The complex, which was obtained by evaporation of the benzene extract, was recrystallized from benzene-ligroin. m.p., 134-0-134.5°.

Palladium acetate was prepared from Pd sponge and glacial AcOH in the presence of HNO_3 according to the procedure of Wilkinson et al.⁵

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