

Reaction of Styrene with Palladous Salts — Product Control by Anions and Cupric Salts[†] —

Sakae UEMURA* and Katsuhiko ICHIKAWA**

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By the reaction of styrene with palladium (II) chloride in acetic acid containing copper (II) chloride and sodium acetate (molar ratio, 2 : 1) at 75°C, α -chloro- β -acetoxyethylbenzene and α,β -diacetoxyethylbenzene (saturated products) were obtained. When the molar ratio of the added salts was 1 : 2, the main product was β -acetoxy styrene (unsaturated product). These results have been explained as follows. The unsaturated product results from the oxypalladate, which is formed by the reaction of styrene-palladium (II) chloride π -complex with the acetate anion, through simultaneous depalladation and deprotonation. The saturated products are formed by the reaction of the same oxypalladate with copper (II) chloride and the chloride ion, and by subsequent acetolysis. Oxidation with palladium (II) acetate (through oxypalladation) gave α - and β -acetoxy styrene and no saturated products.

INTRODUCTION

Many papers have been published on the synthetic and kinetic studies on the reaction of olefins with palladium (II) salts since the aldehyde synthesis by Höchst-Wacker method was reported, and it is concluded generally that the reactions proceed through the nucleophilic attack of various reagents on olefin-palladium (II) salt π -complexes.¹⁾ The formation of acetoxy derivatives of 2- and 3-cyclohexenol from cyclohexene²⁾ and chloroacetoxy norbornane from norbornene³⁾ by the reactions in acetic acid containing palladium (II) chloride, sodium acetate and copper (II) chloride, has been explained to be the results of the reaction of oxypalladium compounds which were formed from palladium π -complexes. Kitching, Rappoport and Winstein proposed oxypalladation-depalladation with simultaneous deprotonation mechanism for the allylic oxidation of olefins with palladium (II) acetate.⁴⁾ In the present paper, the oxidation of styrene has been studied in order to clarify the relationships between the formation of vinyl acetate and the saturated chloroacetoxy compound and between the reaction of π -complex and oxymetallation. It is well known that acetophenone is formed by the reaction of styrene with palladium (II) salts in aqueous solution and the kinetics in aqueous tetrahydrofuran has been reported by Hashimoto and Okada.⁵⁾ The present authors studied the oxidation of styrene in anhydrous acetic acid, in particular, the effects of anions and copper (II) salts on the product distributions.

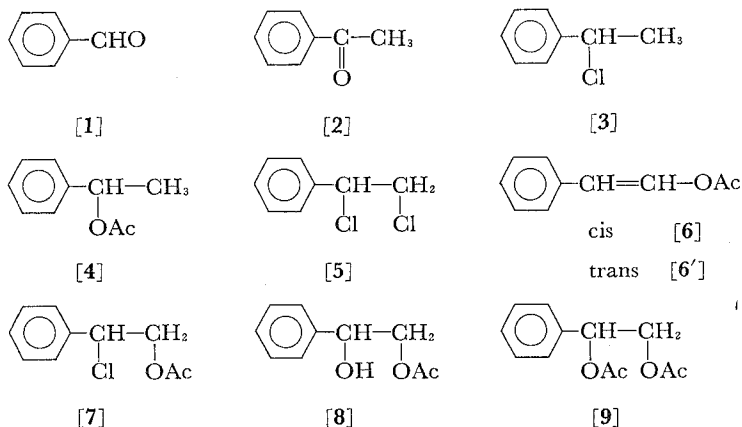
[†] translated from *Nippon Kagaku Zasshi*, **88**, 893 (1967).

* 植村 栄: Laboratory of Petroleum Chemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto.

** 市川克彦: Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto.

RESULTS

Into acetic acid solutions containing palladium (II) chloride, sodium acetate and copper (II) chloride or acetate at 75–80°C, styrene was added under stirring. Work-up of the reaction mixture gave the following products [1–9], including those by side reactions. The amounts of [1] and [2] were only a little, and [3]–[5] are the products by side reactions. [6]–[9] are the products by the reaction of palladium (II) salt.



Effects of mole ratio of sodium acetate and copper (II) chloride. The results of the reactions of acetic acid solutions containing styrene (0.2 mole), palladium (II) chloride (1 g., 0.006 mole) and sodium acetate and copper (II) chloride in various ratios at 75°C are listed in Table 1. The yields of the products were calculated on the basis of the amounts of copper (II) chloride consumed, since the palladium formed was assumed to be oxidized by copper (II) chloride. In the case of 1 : 2 mole ratio of sodium acetate and copper (II) chloride, the increase of the reaction time resulted in the increases of the yields of 5, 7 and 9 and the decrease of that of 8 (Exp. 1, 2 and 3). 8 appears to be formed by the reaction of water contained in acetic acid or other reagents and to be changed to 9 under the catalysis of hydrochloric acid formed. The yields of 7 tend to decrease with the increase of the reaction time and it was confirmed by a separate experiment that 7 is converted to 9 and other unidentified products. It was also confirmed that 5 does not form 6–9 under the conditions. In the absence of sodium acetate, a large amount of 4 which is the addition product between styrene and acetic acid was formed, and 6–9 associated with palladium (II) salt were little obtained (Exp. 6). It is concluded, therefore, that the oxidation of styrene with palladium (II) salt in acetic acid does not proceed in the absence of sodium acetate. When the reaction was carried out with different mole ratios of sodium acetate and copper (II) chloride at 75°C for 8 hr, it was observed that the products were different from those described above (Exp. 4 and 5). With the mole ratio of 2 : 1, the yields of 5 and 7–9 were only traces and an unsaturated product, β -acetoxystyrene (cis 6 and trans 6') was the main product. As is mentioned later, 6 and 6' are formed in the reaction system without copper (II) salt. The ratio of 6 and 6' was 1 : 2.5–3. In the case of mole ratio of

Table 1. Reaction Conditions and the Products (HOAC 300 ml, PdCl₂ 1 g, 75°C).

Exp. No.	Reaction Conditions					React. Time (hr)	Recovered Styrene	Products g (yield %)									Cu ²⁺ consumed (%)
	Styrene (g)	NaOAc (g)	CuCl ₂ (g)	LiCl (g)	3			4	5	6	6'	7	8	9			
1	20	16.5 (0.2 mol)	54 (0.4 mol)	—	8	3.6	—	—	6.4 (47.8)	—	—	4.2 (27.1)	1.8 (12.8)	1.4 (8.1)	39		
2	20	16.5	54	—	16	2.8	—	—	8.2 (30.3)	—	—	8.1 (26.5)	1.2 (4.3)	2.1 (6.1)	77		
3	20	16.5	54	—	64	1.7	—	0.6	13.7 (52.2)	—	—	7.9 (26.5)	—	6.2 (18.6)	75		
4	20	16.5	27	—	8	6.9	0.3	0.6	1.8 (11.3)	0.9 (6.1)	2.4 (16.3)	1.3 (7.2)	1.5 (9.2)	1.5 (7.4)	91		
5	20	33	27	—	8	7.0	0.4	0.4	trace	1.4 (21.2)	3.2 (48.2)	0.3 (3.7)	0.3 (4.1)	0.3 (3.3)	41		
6	20	—	50	—	16	7.9	0.4	4.6	0.7	—	—	—	—	0.3	27		
7	20	16.5	CuCl ₂ ·2H ₂ O 68.2(0.4 mol)	—	8	1.8	—	2.0	11.1 (42.3)	—	—	1.9 (6.4)	—	5.8 (17.4)	75		
8	20	16.5	Cu(OAc) ₂ 50	17	16	5.7	—	2.0	1.7	0.4	1.3	0.4	1.2	2.4	—		
9	10	16.5	—	17	8	4.0	—	0.2	—	0.1	0.15	—	—	—	—		

sodium acetate to copper (II) chloride is unity, both **6** and **6'** and **7-9** were formed as was expected.

With hydrated copper (II) chloride, the reaction was almost complete after 8 hr (Exp. 7), and **5** and **9** were the main products. Elongation of the reaction time resulted in increases of the yields of **3** and **4**.

In order to clarify the effects of the anion on the product distribution, experiments with copper (II) acetate in place of copper (II) chloride were conducted in the presence of lithium chloride (molar ratio of acetate and chloride ion was approximately unity). The product distribution (Exp. 8) was almost the same with that of Exp. 4. The products of the reaction in the presence of lithium chloride and sodium acetate and in the absence of copper (II) salt were **6** and **6'** and the formation of **7-9** was not observed (Exp. 9).

Oxypalladation and related reaction; (See Table 2). The reaction of styrene and palladium (II) chloride without copper (II) chloride gave β -acetoxystyrene (Exp. 10) and the addition of copper (II) acetate in this system resulted in the increase of the yield (Exp. 11). When sodium acetate was not used in this reaction system, the formation of α -acetoxystyrene as well as **6** and **6'** was observed (Exp. 12). Since these products appear to have resulted from oxypalladation reaction, an experiment with palladium (II) acetate was conducted with the result that the products were the same (Exp. 13). The yields of α -acetoxystyrene, **6** and **6'** were 9, 11 and 19% respectively and the product ratio was about the same with that of Exp. 12.*

Side reaction. The formation of **3** and **4** appears to be independent from the reaction of palladium (II) chloride-styrene π -complex, since 0.4 g of **3** and 0.9 g of **4** were obtained by the reaction (75°C, 16 hr) of 10 g of styrene in acetic acid added with the same quantity of hydrochloric acid (6 mmol) corresponding to that of palladium (II) chloride. **5** was found to be formed by the reaction of copper (II) chloride and styrene in acetic acid containing sodium acetate. This chlorination reaction will be reported in a separate paper.**

Table 2. Reaction Conditions and the Products.

Exp. No.	Reaction conditions							Products (g)		
	Styrene (g)	HOAc (ml)	NaOAc (g)	Cu(OAc) ₂ (g)	PdCl ₂ (g)	React. Temp. (°C)	React. Time (hr)	Recovered Styrene	6	6'
10	10	100	8	—	1	75	18	4.3	trace	0.53
11	20	200	16.5	50	1	75	18	10.7	0.34	1.4
12	10	100	—	25	1	75	18	3.8	0.05	0.17*
13	5	100	—	—	Pd(OAc) ₂ 1	75	18	2.3	0.08	0.14*

* About equal amount of α -acetoxystyrene to **6** was obtained.

* The detailed report of this paragraph had been published in *Nippon Kagaku Zasshi*, **89**, 692 (1968). The main product was the oxidative coupling product of styrene, 1,4-diphenyl-1,3-butadiene.

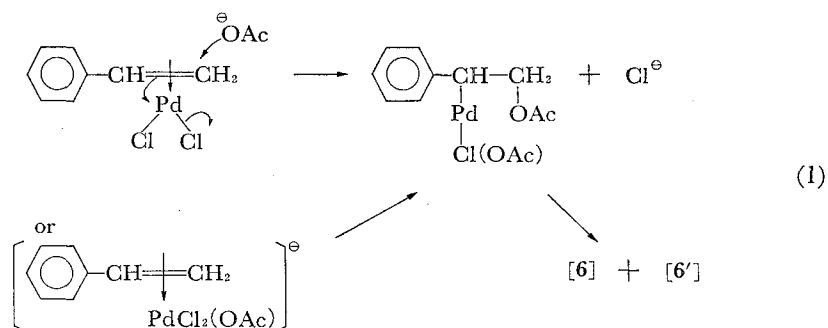
** The detailed reports had been published in *Kogyo Kagaku Zasshi*, **71**, 1657 (1968) and *Bull. Japan. Petrol. Inst.*, **12**, 77 (1970).

DISCUSSION

Papers published on the oxidation of olefins with palladium (II) salt so far report that only unsaturated compounds including carbonyl compounds are formed. This is the same in the case of recently reported oxypalladation reaction.⁴⁾ Only one exception which reports the formation of saturated compound is that by Baird mentioned in the introduction. The results presented here show clearly that the same reaction system can give either saturated or unsaturated products depending on the reaction conditions.

In the oxidation of cyclohexene in HOAc-NaOAc-CuCl₂ system, Green proposed²⁾ that one of the chlorine atoms of olefin-palladium (II) chloride π -complex is replaced by acetoxy group, this acetoxy group forms a bond with olefinic carbon to give oxypalladation type product intramolecularly and the final products are formed through hydride shift followed by depalladation and deprotonation. On the other hand, Baird assumed that acetoxy anion attacks directly the π -complex to form oxypalladation type σ -complex in the reaction of norbornene. Thus, it is assumed generally that the reaction proceeds through the formation of σ -complex from π -complex, although the mechanism of the formation of the former is not yet clear.

The experimental results mentioned above show that the reaction does not proceed in the absence of acetate anion. This appears to show that acetate anion attacks π -complex to form oxypalladation product as the intermediate. Comparing the results of Exp. 4 and 5, vinyl type products are formed in the reaction where the concentration of acetate anion seems to be higher. It is likely, therefore, that the oxypalladation product is formed in the case of higher concentration of acetate anion and the products are those which are characteristic to oxypalladation reaction (eq. 1).

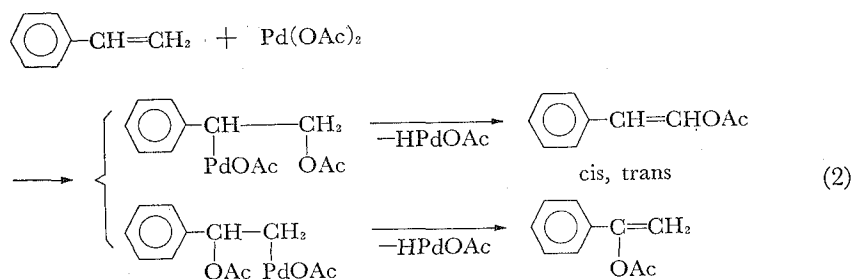


When the concentration of copper (II) chloride was higher than that of sodium acetate, the formation of saturated compounds of 7-9 was observed. In a similar reaction system, Baird assumed that the saturated product is formed by the attack of chloride anion on the carbonium ion which is formed by the separation of acetoxy group from σ -complex (oxypalladate). Considering, however, that the stronger nucleophile, acetate anion should attack the carbonium ion more effectively than chloride ion to form acetoxyated compound in place of chloride, this explanation have to be reexamined. The fact that no product of chloride nor other saturated product were obtain-

ed even in the presence of added lithium chloride (Exp. 9) shows that Baird's explanation must be corrected. The present results suggest that the formation of saturated product requires the presence of both copper (II) salt and chloride ion, and is resulted possibly through the interaction of palladium in oxypalladate with copper and intramolecular attack of chloride ion on carbon. **8** and **9** are the solvolysis products of **7** and this was confirmed by separate experiments.

According to the paper by Green *et al.*, the reaction of cyclohexene did not give the saturated products at 20°C, although the details of the experiments were not described. Our experiments of the same reaction at 75°C showed that saturated chloro- and acetoxy-products as well as vinyl type one are formed.* This might be due to the differences of the reaction temperature.

In contrast with the cases with copper (II) chloride where only β -acetoxy-styrene was obtained, α -acetoxy-styrene as well as β -derivative was obtained in the case with copper (II) acetate (Exp. 12). This appears to be resulted from the oxypalladation of styrene with palladium (II) acetate which was formed by the substitution of chloride with acetate and the reaction does not involve the π -complex formation. The oxypalladation can be represented by equation 2. Considering the product ratio, the oxypalladate in which palladium is bonded to α -carbon is formed more favorably than



the other. In the case of oxymercuration and oxythallation, the metals form bonds with terminal carbon.^{6,7)} In the case of lead tetraacetate, however, the possibility of the addition of lead atom to α -carbon (7% at most) is shown in the oxidation of *p*-methoxystyrene.⁸⁾ Thus, it is clear that the orientation in oxymetallation depends on the kind of metal. This problem is under investigations.

EXPERIMENTAL

Materials. Styrene was distilled just before use and other commercial reagents were used without purification. Palladium (II) acetate was prepared by the reported method⁹⁾ from palladium (II) nitrate and acetic acid.

Procedure. Styrene was added dropwise under stirring at reaction temperature into a four necked 500 ml flask equipped with stirrer, thermometer, reflux condenser and dropping funnel containing PdCl₂, CuCl₂, NaOAc and HOAc. The reaction mixture was kept for appropriate times. After cooling and filtration the filtrate

* unpublished data.

was diluted with water and extracted with benzene. The extract was washed with sat. aqueous NaHCO_3 and dried over Na_2SO_4 and distilled. The amount of Cu^{2+} in precipitates and water layer were determined by iodometry.¹⁰⁾

Identification of the reaction products and determination of the composition were carried out on a gas chromatography (HITACHI F-6; carrier gas, N_2 30 ml/min) using Apiezon-L 1 m and SE-30 (5% on Celite) 1 m columns, and by IR (JASCO IR-S) and NMR (JEOL JNM-3H-60; CDCl_3 solvent, TMS as internal standard) spectra.

Identification of products.

Acetophenone [2]: 2,4-Dinitrophenylhydrazone, mp 245–247°C; mixed mp with authentic sample (mp 248°C) was 246–248°C.

α -Chloroethylbenzene [3]: Bp₁₃ 60–88°C. Retention time of g.l.c. and IR spectra were the same as the authentic sample.

α -Acetoxyethylbenzene [4]: Bp₁₀ 75–82°C. Retention time of g.l.c. and IR spectra were the same as the authentic sample. NMR τ 8.50 (d. 3H), 7.98 (s. 3H), 4.12 (q. 1H), 2.70 (s. 5H).

Styrenedichloride [5]: Bp₁₄ 110.5–112°C, n_D^{15} 1.5520 (lit.¹¹⁾ bp₁₅ 114.5–115.5°C, n_D^{20} 1.5544). NMR τ 6.15 (2H)*, 5.08 (1H)*, 2.70 (s. 5H).

β -Acetoxystyrene [6], [6']: Bp₃ 84–90°C. IR spectra showed strong absorption (vinyl ester) at 1770, 1665, 1220, 1105 and 945 cm^{-1} other than the one due to benzene ring. Retention time of g.l.c. and IR spectra were different with the authentic α -acetoxystyrene. NMR of **6** τ 7.77 (s. 3H), 4.32 (d. $J=7$ cps 1H, lit.¹²⁾ τ 4.43), 2.65 (m. 5H), 2.60 (d. $J=7$ cps, 1H, lit. τ 2.65). NMR of **6'** τ 7.85 (s. 3H), 3.65 (d. $J=13$ cps, 1H, lit. τ 3.72), 2.77 (m. 5H), 2.20 (d. $J=13$ cps, 1H, lit. τ 2.23).

Hydrogenation of 6 and 6': A mixture of 20% of **6** and 80% of **6'** (0.410 g) was hydrogenated at room temperature with 0.5 g of Pd-BaSO₄ catalyst in 50 ml methanol. After 3 hr 97 ml (1.7 mol eq.) of H₂ was absorbed and 0.245 g of product was obtained by distilling off methanol. It was consisted of 41.2% of 2-phenylethyl alcohol [**10**] and 58.8% of 1-acetoxy-2-phenylethane [**11**] and none of **6** and **6'** was detected. When hydrogenation was stopped at 3 minutes 1.2 mol eq. of H₂ was absorbed and the ratio of **10** and **11** was nearly the same as in the case of 3 hr's reaction. **10** was isolated by distillation in pure form: bp₁₄ 100–104°C (lit.¹³⁾ bp₁₄ 104°C).

α -Chloro- β -acetoxyethylbenzene [7]: NMR τ 7.98 (s. 3H), 5.60 (d. $J=7$ cps, 2H), 4.95 (t. $J=7$ cps, 1H). The reaction of silver acetate (4g) and a mixture of 9% of **5**, 72% of **7** and 19% of **9** (3.5 g) in 50 ml acetic acid at 105°C for 12 hr gave 3.6 g of **9**; bp₃ 123–124°C.

α -Hydroxy- β -acetoxyethylbenzene [8]: IR spectrum of a mixture of **8** and **9** showed strong absorption due to hydroxyl group. NMR τ 8.02 (s. 3H), 7.00 (s. 1H), 5.91 (d. $J=8$ cps, 1H), 5.89 (d. $J=5$ cps, 1H), 5.15 (q. 1H), 2.78 (s. 5H). The peak at τ 7.00 vanished in D₂O solvent. The reaction of a mixture of 55.6% of **8** and 44.4% of **9** (3 g) with 2 g of acetic anhydride in 10 ml of pyridine at 85°C for 3 hr gave 2.5 g of **9**; bp_{2.5} 124–125°C, n_D^{19} 1.5040.

* AB₂ type splitting

α,β -Diacetoxyethylbenzene [9]: Bp₂ 114–115°C, n_D²⁰ 1.5110. Retention time of g.l.c. and IR spectra were the same as the authentic sample. NMR τ 7.98 (s. 3H), 7.92 (s. 3H), 5.72 (d. J=6 cps, 2H), 4.00 (q. J=6 cps, 1H), 2.70 (s. 5H).

Authentic samples.

3 was prepared by heating 1-phenylethanol and conc. HCl at 80°C for 2 hr; bp₁₄ 75–79°C, n_D¹⁸ 1.5324 (lit.¹⁴) n_D¹³ 1.5337). **4** was prepared by heating 1-phenylethanol and acetic acid in the presence of small amount of conc. H₂SO₄; bp₁₃ 100–120°C. **9** was prepared by heating styrene and thallium (III) acetate in acetic acid⁷⁹; bp₅ 130–134°C. α -Acetoxystyrene was prepared from phenylacetylene and acetic acid by mercury (II) acetate catalyst; bp₄ 86–89°C, n_D²⁰ 1.5333 (lit.¹⁵) n_D²⁰ 1.5329).

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