

## The Intramolecular Cyclization Reaction of Unsaturated Acid with Palladium(II) Salt

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**Synopsis.** The stoichiometric reaction of sodium salts of 3-butenic acid, 3-pentenoic acid, 4-pentenoic acid, and 4-hexenoic acid with lithium tetrachloropalladate(II) affords 2-buten-4-olide, 4-methyl-2-buten-4-olide (**2b**), **2b**, and 4-ethyl-2-buten-4-olide respectively. Similarly, the reaction of 2-styrylbenzoic acid with palladium(II) salt leads to the formation of 3-phenylisocoumarin.

It is well known that most of the 2-buten-4-olides can be synthesized by the dehydrohalogenation of  $\alpha$ -halobutyrolactones,<sup>1)</sup> by the lactonization of  $\gamma$ -keto-acids,<sup>2)</sup> or by the oxidation of  $\alpha,\beta$ -unsaturated esters with selenium dioxide.<sup>2,3)</sup> Recently, an intramolecular cyclization of olefinic compounds *via* oxypalladation<sup>4-6)</sup> has received wide attention. In relation to these reactions, we wish to report herein the palladium-induced intramolecular cyclization of both 3-butenic acids and 4-pentenoic acids to 2-buten-4-olides.

The sodium salts of 3-butenic acid (**1a**) and 3-pentenoic acid (**1b**) were treated with lithium tetrachloropalladate(II) in water to produce 2-buten-4-olide (**2a**) and 4-methyl-2-buten-4-olide ( $\beta$ -angelica lactone) (**2b**) in 38 and 32% yields respectively. In the reactions of both **1a** and **1b** with palladium(II) salt, no formation of 3-buten-4-olide derivatives was observed. Henry and Ward<sup>7)</sup> have reported that the reaction of cyclohexene with palladium(II) acetate gave products which were

consistent with a *trans* acetoxypalladation, followed by Pd(II)-hydride elimination and readdition. In the reaction of **1a** and **1b** with palladium(II) salt, the formation of **2a** and **2b** can be explained by the Scheme 1, involving intramolecular oxypalladation to give the intermediate (**3**), followed by the  $\beta$ -elimination of the HPdCl species.

Furthermore, under the same conditions, 4-pentenoic acid (**1c**) and 4-hexenoic acid (**1d**) afforded **2b** and 4-ethyl-2-buten-4-olide (**2c**) in 38 and 30% yields respectively. In the reactions of both **1c** and **1d** with palladium(II) salt, no formation of the six-membered ring products was observed. The results are summarized in Table 1.

Hosokawa *et al.*<sup>4f)</sup> have recently reported the regioselectivity of the palladium(II)-induced intramolecular cyclization of 2-(3-methyl-2-butenyl)phenol. However, in the reaction of **1c** and **1d** with palladium(II) salt, the formation of the five-membered ring products indicated that the cyclization of **1c** and **1d** involves a preferential attack of the oxygen atom of the carboxyl group on the 4-position of unsaturated acid (**1c** or **1d**), followed by a Pd(II)-hydride elimination-readdition process (see Scheme 1).

On the other hand, the reaction of 1-cyclohexenyl-acetic acid (**1e**) with palladium(II) salt led to the formation of a mixture of 5,6,7,7a-tetrahydro-2(4*H*)-benzofuranone (**2d**) and 4,5,6,7-tetrahydro-2(3*H*)-benzofuranone (**2e**). Similarly, the reaction of 2-vinylbenzoic acid (**1f**) and 2-styrylbenzoic acid (**1g**)

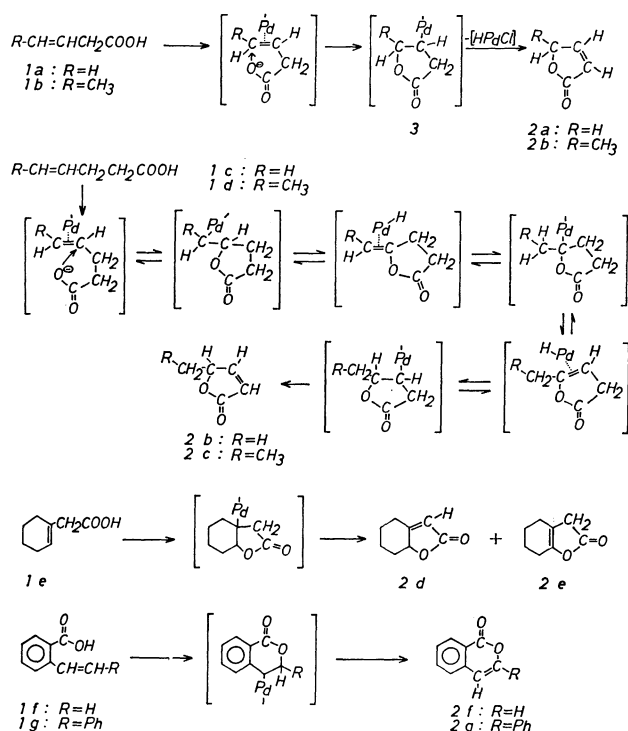


Fig. 1.

TABLE 1. REACTION OF UNSATURATED ACID (**1**) WITH LITHIUM TETRACHLOROPALLADATE(II)

Substrate	Solvent	Product (yield, %)
<b>1a</b>	H <sub>2</sub> O	<b>2a</b> (R=H) <sup>a)</sup> (38%)
<b>1b</b>	H <sub>2</sub> O	<b>2b</b> (R=CH <sub>3</sub> ) <sup>b)</sup> (32%)
<b>1c</b>	H <sub>2</sub> O	<b>2c</b> (R=H) (38%)
<b>1d</b>	H <sub>2</sub> O	<b>2b</b> (R=CH <sub>3</sub> ) <sup>c)</sup> (30%)
<b>1e</b>	H <sub>2</sub> O	<b>2d</b> <sup>d)</sup> (28%) + <b>2e</b> <sup>e)</sup> (10%)
<b>1f</b>	H <sub>2</sub> O-dioxane	<b>2f</b> (R=H) <sup>f)</sup> (46%)
<b>1g</b>	H <sub>2</sub> O-dioxane	<b>2g</b> (R=Ph) <sup>g)</sup> (42%)

a) Bp 90—92 °C/16 Torr, (lit.<sup>h)</sup> bp 107—109 °C/24 Torr). b) Bp 78—80 °C/5 Torr, (lit.<sup>i)</sup> bp 208 °C). c) Bp 85—86 °C/5 Torr, (lit.<sup>j)</sup> bp 72 °C/1.5 Torr). d) Bp 115—117 °C/5 Torr, (lit.<sup>k)</sup> bp 108—108.5 °C/1 Torr). e) Bp 92—95 °C/3 Torr, (lit.<sup>l)</sup> bp 88—93 °C/1 Torr). f) Mp 47 °C, (lit.<sup>m)</sup> mp 45—46 °C). g) 88—90 °C, (lit.<sup>n)</sup> mp 89—90 °C). h) C. C. Price and J. M. Judge, *Org. Synth.*, **45**, 22 (1965). i) F. A. Kuehl, Jr., R. P. Linstead, and B. A. Orkin, *J. Chem. Soc.*, **1950**, 2213. j) C. Schöpf and R. Kühne, *Chem. Ber.*, **83**, 390 (1950). k) S. Siegel, S. K. Coburn, and D. R. Levering, *J. Am. Chem. Soc.*, **73**, 3163 (1951).

with palladium(II) salt afforded isocoumarin (**2f**) and 3-phenylisocoumarin (**2g**) respectively. The palladium-promoted reaction of **1e**, **1f**, and **1g** also proceeds via an intramolecular oxypalladation, followed by an elimination of HPdCl.

### Experimental

**Materials.** The following compounds were synthesized by the methods described in the literature: 3-butenic acid (**1a**),<sup>8)</sup> 3-pentenoic acid (**1b**),<sup>9)</sup> 4-pentenoic acid (**1c**),<sup>10)</sup> 4-hexenoic acid (**1d**),<sup>11)</sup> 1-cyclohexenylacetic acid (**1e**),<sup>12)</sup> 2-vinylbenzoic acid (**1f**),<sup>13)</sup> and 2-styrylbenzoic acid (**1g**).<sup>14)</sup>

**General Procedure for The Reaction of Unsaturated Acid with Palladium(II) Salt.** A solution of 10 mmol of unsaturated acid and 5 mmol of sodium carbonate in water (50 ml) or dioxane-water (1 : 1, 50 ml) was stirred with 10 mmol of lithium tetrachloropalladate(II) at room temperature. After stirring for 24 h, the reaction mixture was then extracted with ether. The ether extract was washed with aqueous sodium hydrogencarbonate and dried over anhydrous magnesium sulfate. After the evaporation of the solvent, the product was isolated by distillation or by column chromatography on silica gel. The structures of the products were confirmed by a mixed-melting-point determination, by comparing the retention times on gas chromatograms, and by the observation of the IR and NMR spectra.

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