

## Palladium-catalysed Conversion of Alkenols into Five- and Six-membered Ring Lactones at Room Temperature and Atmospheric Pressure

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Unsaturated alcohols react with carbon monoxide, oxygen, palladium chloride, copper(II) chloride, and hydrochloric acid in tetrahydrofuran to give lactones in 42–80% yield.

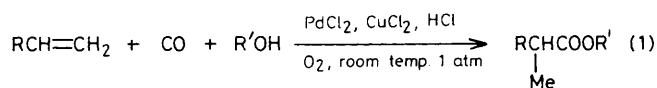
Palladium chloride catalyses the hydroesterification and hydrocarboxylation of olefins under remarkably mild conditions (equation 1).<sup>1,2</sup> The oxidative carbonylation reaction is regiospecific in the case of water and mono alcohols such as methanol, and regioselective when diols are employed as the reaction media.<sup>3</sup>

It seemed conceivable that appropriate unsaturated alcohols could undergo intramolecular reaction affording lactones. The recent report by Semmelhack and Bodurow<sup>4</sup> on the intramolecular alkoypalladation-carboxylation of unsaturated alcohols to tetrahydrofuran and tetrahydropyran esters using neutral conditions and no oxygen, prompts us to disclose our results in this area.

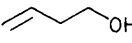
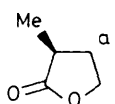
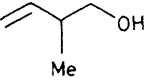
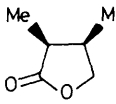
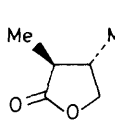
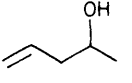
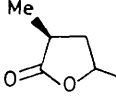
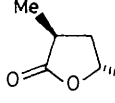
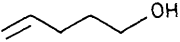
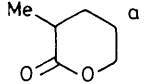
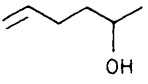
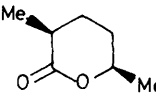
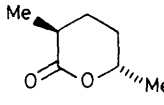
Treatment of but-3-en-1-ol with carbon monoxide, palladium chloride, copper(II) chloride, concentrated hydrochloric acid, and oxygen in dry tetrahydrofuran (THF) gives  $\alpha$ -methyl- $\gamma$ -butyrolactone in 60% yield. A 2:1 mixture of *trans:cis*-2,3-dimethyl- $\gamma$ -butyrolactone was obtained from 2-methyl-but-3-en-1-ol (Table 1). Isomeric 2,4-dimethyl- $\gamma$ -butyrolactones were formed from pent-4-en-2-ol, while six-

membered ring lactones ( $\delta$ -valerolactones) were isolated using substrates in which there are three methylene groups between the hydroxy and olefinic functionalities. All of these reactions occurred at room temperature and one atmosphere pressure.

A recent elegant study by Samsel and Norton<sup>6</sup> showed that the complex  $(PPh_3)_2Pd(Cl)CO_2CH_2CH_2CH=CH_2$ , on heating in toluene at 100°C for 24 h, gave the unsaturated  $\alpha$ -methylene- $\gamma$ -butyrolactone in 42% yield (HCl was also present). However, similar thermolysis of  $(PPh_3)_2Pd(Cl)CO_2[CH_2]_3CH=CH_2$  did not yield any identifiable insertion product. This behaviour is different from the process described herein whereby lactones were isolated from olefinic alcohols in which the two functionalities are separated by either two or three methylene groups. In spite of these



**Table 1.** Palladium-catalysed intramolecular cyclization of unsaturated alcohols.

Reactant	Products	Yield / %
		60
	 (33)  (67)	42
	 (50)  (50)	80
		75
	 (38)  (62)	50

<sup>a</sup> Identified by comparison of data [g.c. retention time, i.r., n.m.r. (<sup>1</sup>H, <sup>13</sup>C), mass spectra] with that for the authentic material.

<sup>b</sup> Isomeric ratios were determined by n.m.r. spectroscopy and by g.c. (ref. 5).

differences, the present reaction may proceed *via* alkoxypalladium and alkoxycarbonylpalladium intermediates, but the mechanism is unknown at present.

This remarkably mild lactone synthesis from olefinic alcohols is clearly superior to other known metal-catalysed routes. For example, cobalt carbonyl catalyses the conversion of methyl substituted but-3-en-1-ols into butyrolactones; however, the yields are modest (3–51%) and drastic conditions are required (300 atm, 240 °C). Rhodium chloride is even less effective.<sup>7</sup> The following general procedure was used: carbon monoxide was bubbled through dry THF (60–70 ml), PdCl<sub>2</sub> (0.140 g, 0.780 mmol) was added, followed by 0.5 ml HCl and copper(II) chloride (0.84 g was used for but-3-en-1-ol and pent-4-en-1-ol; 0.21 g used in the other cases). Oxygen bubbling commenced, the substrate (7.8 mmol) was added, and the reaction mixture was stirred overnight at room temperature. The solution was filtered, and the filtrate was fractionally distilled.

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## References

- 1 B. Despeyroux and H. Alper, *Ann. N.Y. Acad. Sci.*, 1984, **415**, 148.
- 2 H. Alper, J. B. Woell, B. Despeyroux, and D. J. H. Smith, *J. Chem. Soc., Chem. Commun.*, 1983, 1270.
- 3 S. B. Fergusson and H. Alper, *J. Chem. Soc., Chem. Commun.*, 1984, 1349.
- 4 M. F. Semmelhack and C. Bodurow, *J. Am. Chem. Soc.*, 1984, **106**, 1496.
- 5 G. S. Y. Ng, L. C. Yuan, I. J. Jakovac, and J. B. Jones, *Tetrahedron*, 1984, **40**, 1235; S. A. M. Hussain, W. D. Ollis, C. Smith, and J. F. Stoddart, *J. Chem. Soc., Perkin Trans. 1*, 1975, 1480; W. H. Pirkle and P. E. Adams, *J. Org. Chem.*, 1979, **44**, 2169.
- 6 E. G. Samsel and J. R. Norton, *J. Am. Chem. Soc.*, 1984, **106**, 5505.
- 7 J. Falbe, H. J. Schulze-Steinen, and F. Korte, *Chem. Ber.*, 1965, **98**, 886.