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The Pd Catalyzed Reactions of α-Bromo Acrylic acids with 1,3-Dienes to form γ-Lactones

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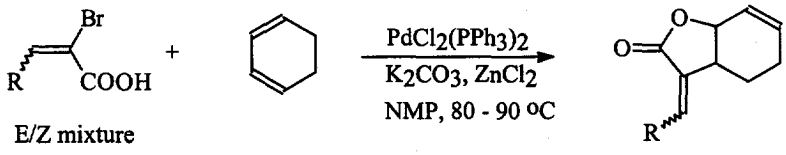
Summary: α-Bromo acrylic acids react with 1,3-dienes in the presence of Pd catalyst, $ZnCl_2$ and a base to give γ- lactones in moderate to high yields.

γ-Lactones are important synthetic intermediates found in several natural products and have been synthesized by different methods.[1] We report in this communication, the reaction of 1,3-dienes with α-bromo acrylic acids to form γ-lactones in moderate to high yields. α-Bromo acrylic acids can be readily prepared from acrylic acids/esters by a bromination-dehydrobromination sequence.

Scheme-1

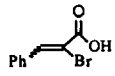
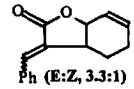
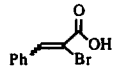
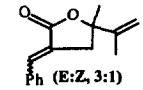


E/Z mixture

R: Ph, 2-Furyl, Me (Z isomer)

The bicyclic lactones formed from cyclohexadiene are cis (J = 6. 35 Hz, ring junction protons). The stereochemistry of the exocyclic olefin in the lactones was confirmed by 2 D - NMR (NOESY experiment)

Table-1 : Pd Catalyzed Reaction of α - Bromo Acrylic Acids with 1,3-Dienes

S. No.	α – Bromo Acid (1a -10a)	1, 3 - Diene	Product (1b - 10b)	Time, h	Yield, %
1	 (Z:E, 1.3:1)		 Ph (E:Z, 3.3:1)	24	61
2			 Ph (E:Z, 3:1)	23	51

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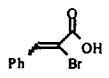
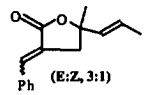
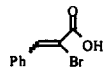
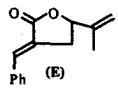
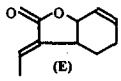
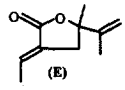
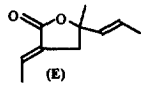
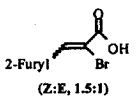
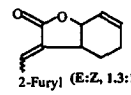
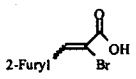
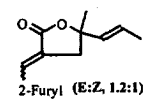
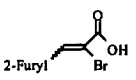
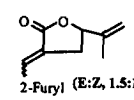
3			 (E:Z, 3:1)	19	61
4			 (E)	2	22
5			 (E)	24	48
6			 (E)	25	55
7			 (E)	23	52
8	 (Z:E, 1.5:1)		 (E:Z, 1.3:1)	6	74
9			 (E:Z, 1.2:1)	24	51
10			 (E:Z, 1.5:1)	10	25

All products were characterized by IR, ^{1}H NMR and MS

of the **Z** isomer of **1b**. Comparison of the chemical shift of the vinylic H with the theoretical values also proved the geometry of the exocyclic olefin.[2]

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References

1. (a) Ito, S.; Kodama, M., Heterocycles, **1976**, 4, 595 (b) Harris, T. M.; Harris, C. M., *Tetrahedron*, **1977**, 33, 2159 (c) Rossi, R.; Bellina, F.; Bechini, C.; Mannina, L.; Veragamini, P., *Tetrahedron* **1998**, 54, 135.
2. Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. Spectrometric Identification of Organic Compounds, John Wiley & Sons, **1974**, 3rd ed., pg 22