

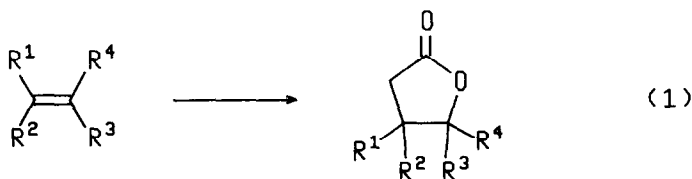
**SYNTHESIS OF  $\gamma$ -LACTONES FROM ALKENES EMPLOYING *p*-METHOXYBENZYL CHLORIDE AS  $^+\text{CH}_2\text{-CO}_2^-$  EQUIVALENT<sup>1</sup>**

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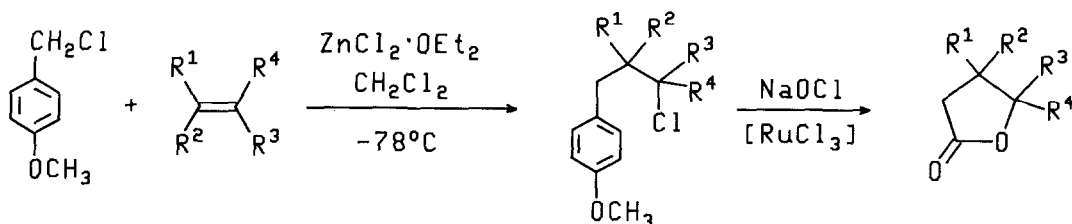
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**Abstract.** The  $\text{ZnCl}_2$  catalyzed reaction of *p*-methoxybenzyl chloride with alkenes yields the 1:1 addition products **3**, which are converted into the  $\gamma$ -lactones **4** via  $\text{Ru(VIII)}$  catalyzed oxidative degradation of the aromatic ring.

The transformation of alkenes into  $\gamma$ -lactones (eq.1) via addition reactions of free radicals has been described by several authors. Boldt performed the conversion (eq.1) by radical initiated addition of bromodicyanomethane towards alkenes and subsequent hydrolysis and decarboxylation.<sup>2</sup> Analogously,  $\gamma$ -lactones were obtained from alkenes and  $\alpha$ -bromocarboxylic acids<sup>3</sup> or the tin salts of  $\alpha$ -iodo or  $\alpha$ -bromoacetic acid.<sup>4</sup> The oxidative addition of carboxylic acids to alkenes, which is achieved in basic medium with metal ions (e.g.  $\text{Mn}^{+++}$ ) as oxidants also involves a free radical addition step.<sup>5</sup> We report now on an electrophilic addition pathway for the transformation (eq.1), which is especially suited for the synthesis of  $\gamma,\gamma$ -bisalkylated  $\gamma$ -lactones.



The  $\text{ZnCl}_2 \cdot \text{OEt}_2$  catalyzed<sup>6</sup> reaction of *p*-methoxybenzyl chloride **1** with the alkenes **2a-f** affords high yields of the 1:1 addition products **3a-f** under conditions analogous to those reported for additions of other  $\text{S}_{\text{N}}1$  active chlorides.<sup>7</sup> For the  $\text{Ru(VIII)}$ -catalyzed oxidations of the aromatic ring,<sup>8</sup> solutions of the crude adducts **3** (10 mmol) in  $\text{CH}_2\text{Cl}_2$  (50 ml) were added dropwise to well stirred mixtures of  $\text{RuCl}_3$  (0.8 mmol),  $\text{CH}_2\text{Cl}_2$  (50 ml) and 140 ml of a 2.16 M aqueous  $\text{NaOCl}$  solution. Satisfactory yields of the lactones **4** are obtained, if the rate of addition of **3** to the oxidants is slow enough to allow the intermediate regeneration of  $\text{RuO}_4$ , which is recognizable by its gold-orange color. The use of acetonitrile as a cosolvent, which has been recommended for related oxidations,<sup>9</sup> was found to diminish the yield of **4**. As expected, the oxidation of the aromatic ring is greatly enhanced by the methoxy group, since the oxidation of **3f** gave 26% of the lactone **4f** (yield not optimized), which incorporates an intact phenyl group.



	1	2				3	4 <sup>a</sup>		
2, 3, 4	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	% Yield	% Yield	<sup>13</sup> C-NMR (CDCl <sub>3</sub> )		
a	H	H	CH <sub>3</sub>	CH <sub>3</sub>	84	54	27.73 (q), 29.38 (t), 34.66 (t), 84.63 (s), 176.74 (s)		
b	H	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	84	69	14.26 (q), 21.63 (q), 27.05 (q), 36.74 (t), 39.87 (d), 86.98 (s), 175.86 (s)		
c	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	88	77	22.99 (q), 23.42 (q), 41.09 (s), 43.88 (t), 88.57 (s), 175.74 (s)		
d	H	H	CH <sub>3</sub>	n-C <sub>3</sub> H <sub>7</sub>	81	59	14.34 (q), 17.20 (t), 25.58 (q), 29.19 (t), 32.95 (t), 43.21 (t), 86.92 (s), 176.90 (s)		
e	H	H	CH <sub>3</sub>	CH <sub>2</sub> -C(CH <sub>3</sub> ) <sub>3</sub>	91	45	26.78 (q), 28.76 (t), 31.12 (s), 31.23 (q), 36.04 (t), 53.44 (t), 88.03 (s), 177.26 (s)		
f	H	H	H	C <sub>6</sub> H <sub>5</sub>	72	26	28.96 (t), 30.98 (t), 81.24 (d), 125.28 (d), 128.45 (d), 128.75 (d), 139.39 (s), 176.93 (s)		

a) <sup>1</sup>H NMR of **4a**: ref.<sup>10</sup>; **4b**, **f**: ref.<sup>2</sup>; **4c**: ref.<sup>11</sup>; **4d** (CDCl<sub>3</sub>): δ 0.95 (t, J = 7.1 Hz, 3 H), 1.35-1.70 (m (4 H) superimposed by s (3 H) at 1.34), 1.95-2.19 (m, 2 H), 2.56-2.66 (m, 2 H); **4e** (CDCl<sub>3</sub>): δ 1.04 (s, 9 H), 1.48 (s, 3 H), 1.65 and 1.75 (AB system with J<sub>AB</sub> = 14.9 Hz, 2 H), 1.80-2.14 (m, 2 H), 2.55-2.65 (m, 2 H).

Preliminary experiments show that an analogous reaction sequence can be carried out with α-substituted benzyl chlorides. The scope of the novel lactone synthesis and of its intramolecular variant is presently under investigation.

**Acknowledgement.** We thank Ms. R. Lammers for exploratory experiments, the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

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(Received in Germany 3 October 1988)