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## Enantioselectivity in the Catalytic Hydroesterification of Acenaphthylene. Direct Evidence of the Racemization of Pd<sup>II</sup>-alkyl species by a Degenerate Substitution Equilibrium with Pd<sup>0</sup>L<sub>n</sub> species.

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Jordi Gironès, Josep Duran, Alfonso Polo, and Julio Real

### General Considerations.

PdCl<sub>2</sub>, Pd(OAc)<sub>2</sub>, PPh<sub>3</sub>, P(*p*-MeC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>, P(*p*-FC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>, rac-BINAP, (*R*)-(+)-BINAP, (*S*)-(-)-BINAP, dppf, MeOH, MeOH-d<sub>1</sub>, Eu(hfc)<sub>3</sub>, *p*-toluenesulfonic acid, HCl (2.0 M in diethyl ether) and CO 4.7 were commercially obtained and used without further purification. Reaction solvents were dried by standard methods and, distilled and deoxygenated before use. Complex [PdCl<sub>2</sub>(PhCN)<sub>2</sub>] were prepared by established procedures.<sup>1</sup> Commercial technical acenaphthylene is of variable quality, containing acenaphthene (15-30%) and some tars. This acenaphthylene was recrystallized in hexane before use. Typically, the recrystallized material has an acenaphthylene content between 88 and 92%, the rest being acenaphthene and uncharacterized materials (2% by GC). NMR spectra were recorded on a Bruker AX-400 or Bruker DPX-200 and reported in the δ scale. <sup>1</sup>H is referenced to tetramethylsilane as internal reference, and the resonance of some added CDCl<sub>3</sub> was used to reference the <sup>2</sup>H spectra. Gas chromatography analyses were performed on a Thermo Quest Trace GC 2000 in a J&W Scientific DB-5 capillary column (30 m x 0,25 mm diameter), incorporating MS detector. Optical rotation of enantiomeric enriched samples of ester **2** in CH<sub>2</sub>Cl<sub>2</sub> solution were measured on a Krüss P3002 electronic polarimeter equipped with a sodium bulb light (589 nm). Flash chromatography was performed on silica gel 60 A CC. Solvents for chromatography were distilled at atmospheric pressure prior to use.

[1] H. M. Colquoum, J. Holton, D. J. Thompson, M. V. Twigg, *New Pathways for Organic Synthesis*, Plenum Press, New York, **1995**, pp 382-383.

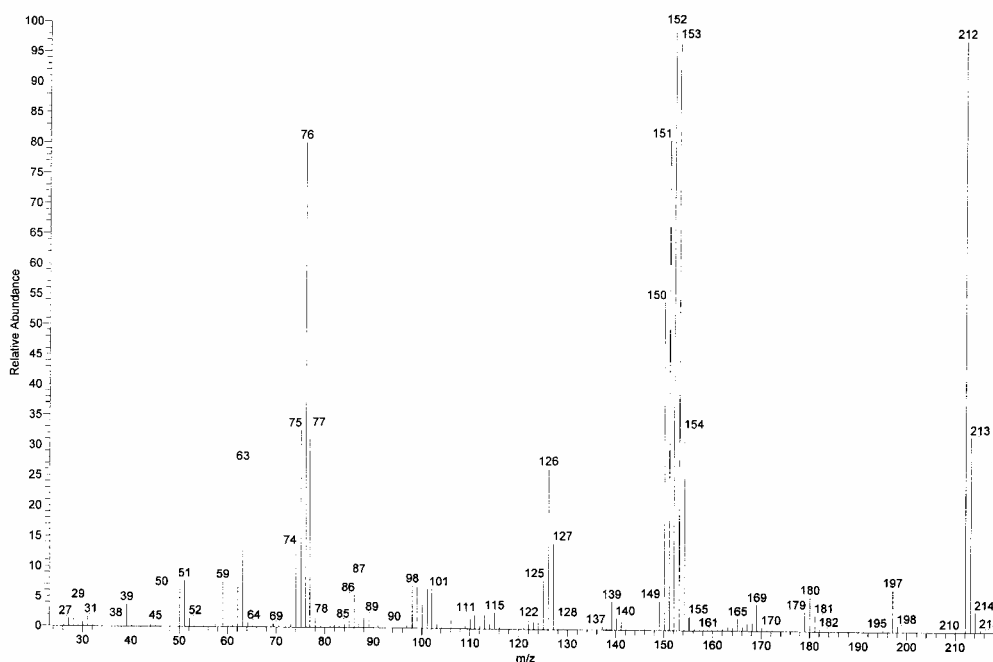


Figure 1. MS of acenaphthene-1-carboxylic acid methyl ester **2-d<sub>0</sub>** obtained by hydroesterification.

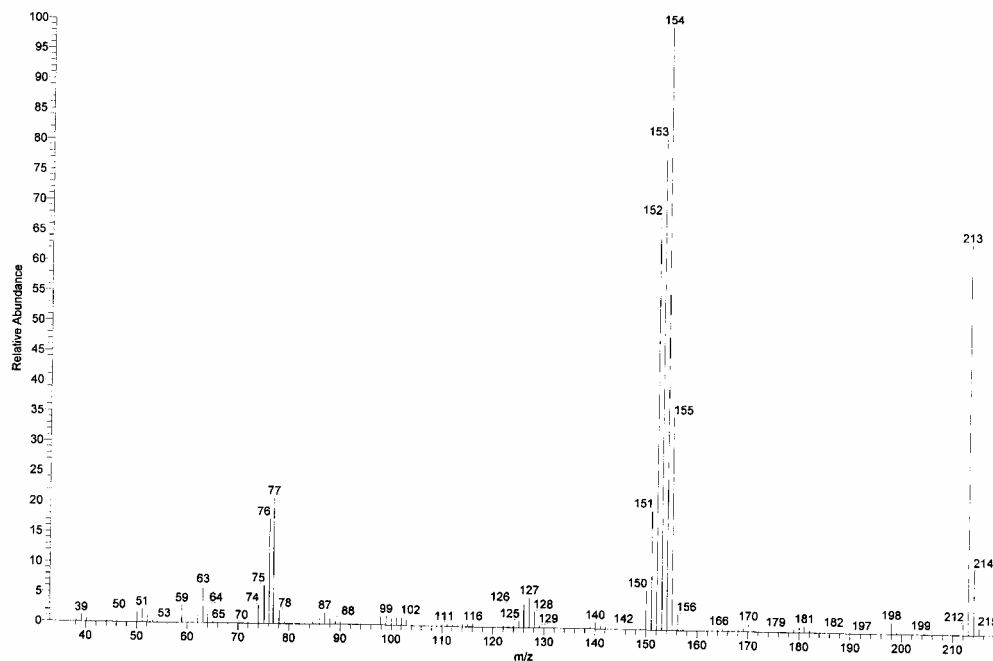


Figure 2. MS of acenaphthene-1-carboxylic acid methyl ester (mainly **2-d<sub>1</sub>**) obtained by deuteroesterification using  $[\text{PdCl}_2(\text{PhCN})_2]$  as catalyst precursor.

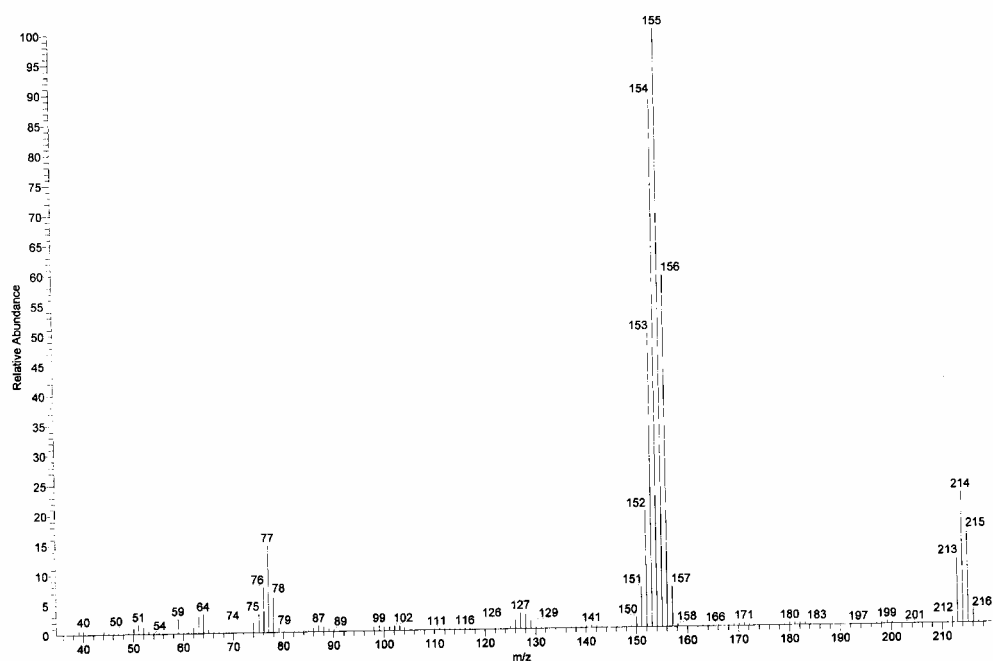


Figure 3. MS of acenaphthene-1-carboxylic acid methyl ester (polydeuterated **2**) obtained by deuterioesterification using  $\text{Pd}(\text{OAc})_2$  as catalyst precursor.

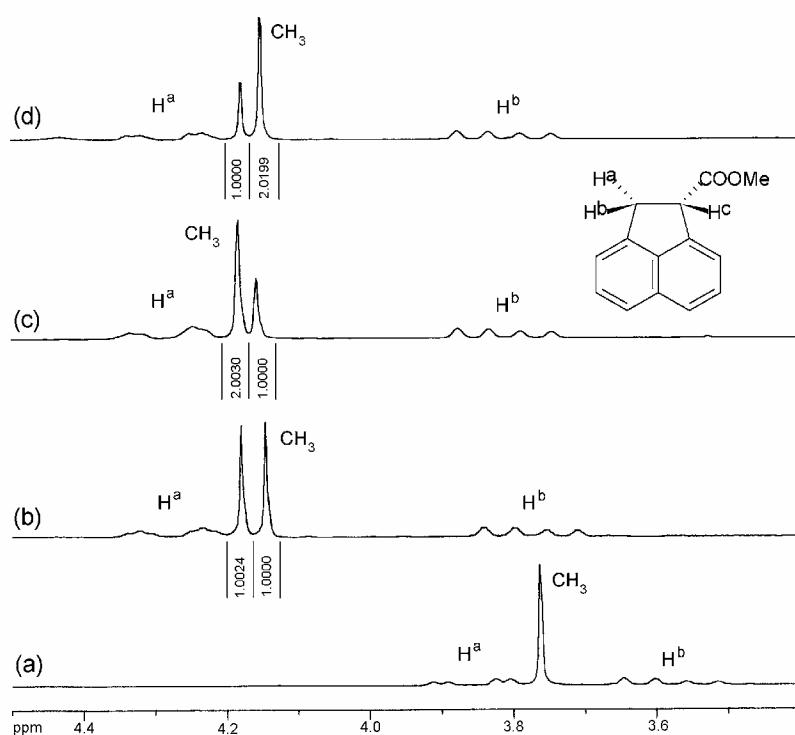


Figure 4.  $^1\text{H}$  NMR of acenaphthene-1-carboxylic acid methyl ester **2**. (a) racemic ester **2**. (b) racemic ester **2** with addition of  $[\text{Eu}(\text{hfc})_3]$ . (c) enantiomeric enriched ester **2**, with addition of  $[\text{Eu}(\text{hfc})_3]$ , obtained using  $\text{Pd}(\text{OAc})_2$  and  $(S)$ -(-)-BINAP. (d) enantiomeric enriched ester **2**, with addition of  $[\text{Eu}(\text{hfc})_3]$ , obtained using  $\text{Pd}(\text{OAc})_2$  and  $(R)$ -(+)-BINAP.

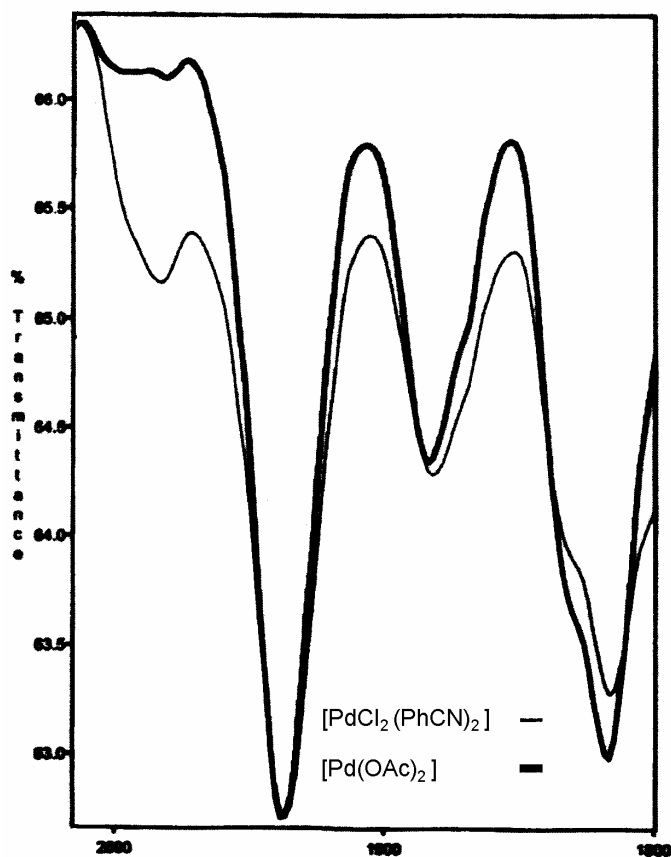


Figure 5. IR spectra of the freshly hydroesterification mixtures using Pd(OAc)<sub>2</sub> and [PdCl<sub>2</sub>(PhCN)<sub>2</sub>] as catalyst precursors.