PETASIS-FERRIER REARRANGEMENT

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What's the Petasis-Ferrier Rearrangement



The stereocontrolled Lewis acid-promoted rearrangement of cyclic enol acetals to the corresponding substituted tetrahydrofurans and tetrahydropyrans is called the Petasis-Ferrier rearrangement.

Mechanism of the Petasis-Ferrier Rearrangement



AIR₃

³R_H

R¹







Type II Ferrier Rearrangement

 R^2



Features of the Petasis-Ferrier Rearrangement



 the configuration of the acetal carbon is retained or enhanced during the rearrangement;
the rearrangement of five-membered enol acetals takes place at a much higher temperature than for the six-membered substrates;

3) trialkylaluminums were found to be the most effective reagents to mediate the rearrangement (*i*-Bu3Al, Me3Al, Me2AlCl being the most common);

4) the stereoselectivity of the aluminum-mediated carbonyl reduction (very last step) depends on the substitution pattern and occurs when *i*-Bu3Al is used (the reduction does not take place with Me2AlCl);

5) a drawback of the procedure is that the olefination step can lead to a mixture of olefin stereoisomers when the applied titanocene is other than dimethyl titanocene

Applications of the Petasis-Ferrier Rearrangement

