Development of Mass Persistent Photoresists

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Introduction

Reasons for Mass Persistent Resist

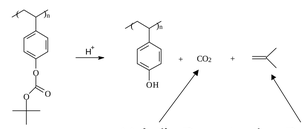
- Current resists are designed to release volatiles
- Outgassing results in film shrinkage
- Volatiles can contaminate optical elements

Design Process for Mass Persistent Resists

Tether the volatile products to the polymer

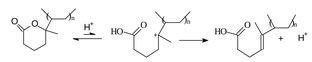
–Design acid labile protecting groups
–Synthesize model compounds
–Test models for functionality
–Polymerize monomer to form mass persistent polymer (resist)
–Lithographic evaluation

t-Boc Protecting Group for 248 nm Resist



Volatile Deprotection Products

Proposed Lactone Ring for Mass Persistent Resist

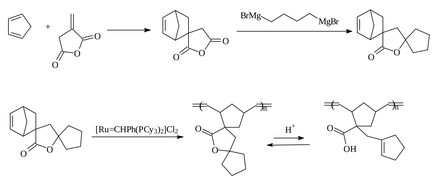


No Volatile Products Produced

Five- and Six-Member Lactones

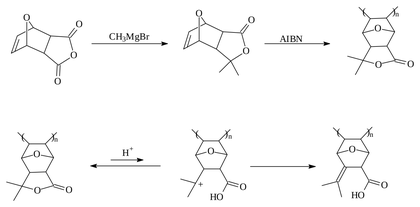
Five and six member lactones failed to ring open under acidic conditions to give the necessary base soluble functional group

Lack of thermodynamic driving force makes equilibrium favor ring closed form

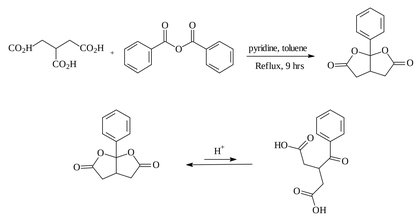


Ring-opening Not Observed by NMR

Synthesis of Model Lactones



Ring-opening Not Observed by NMR



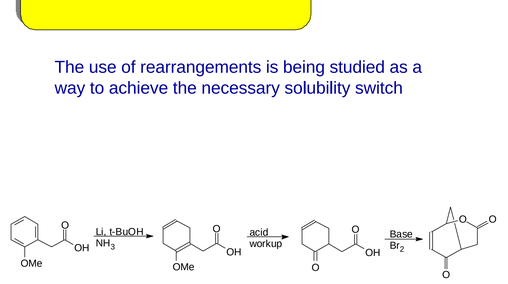
Ring-opening Not Observed by NMR

Canonne, P.; Akssira, M.; Lemay, G. *Tetraheron Letters*, **1981**, *22*, 261.
Canonne, P.; Belanger, D.; Lemay, G. *J. Org. Chem.*, **1982**, *47*, 3953.
Canonne, P.; Akssira, M.; Lemay, G. *Tetrahedron Letters*, **1983**, *24*, 1929.
Canonne, P.; Akssira, M.; Fytas, G.; *Tetrahedron*, **1984**, *40*, 1809.

Chung, K.; Takata., T.; Endo, T. *Macromolecules*, 1995, 28, 3048-3054

Rearrangements

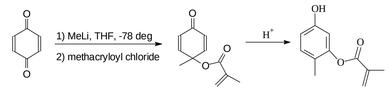
The use of rearrangements is being studied as a way to achieve the necessary solubility switch



Successful ring-opening to two products, one is base soluble

The second product has two base soluble functional groups

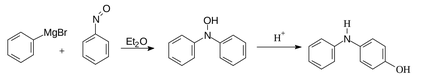
Dienone Phenol Rearrangement



Rearrangement Not Observed by NMR

Microelectronic Tech. Polymers for Advanced Imaging and Packaging, ACS Symp. Series 614, p. 228, 1995.

Bamberger Rearrangement



Rearrangement Not Observed by NMR

J. March, *Advanced Organic Chemistry*. Mc Graw Hill, 1994.

Currently attachment of model compound to polymer is in progress

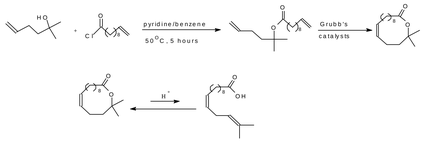
Large and Small Ring Lactones

The ring strain from large and small rings used as a driving force for ring opening

Large ring strain is not sufficient

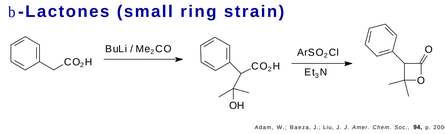
Small ring strain in the β-Lactones pushes equilibrium to ring opened form

Large Ring Lactone (transannular strain)

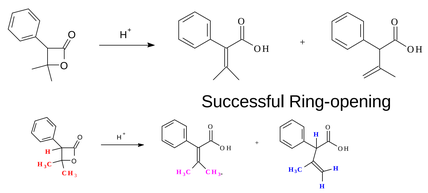


Ring-opening Not Observed by NMR

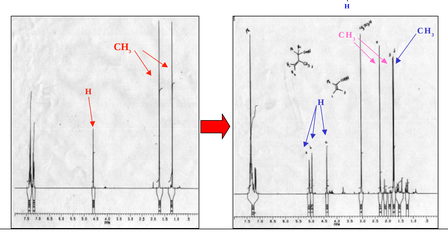
b-Lactones (small ring strain)



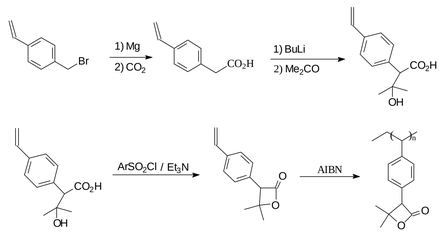
Adam, W.; Baeza, J.; Liu, J. *J. Amer. Chem. Soc.*, **94**, p. 2000, (1972)



Successful Ring-opening



Synthesis of Polymer Based on Model b-Lactone

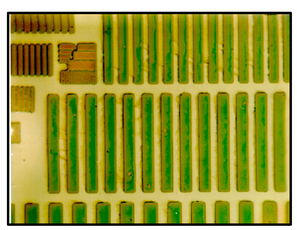


Imaging Result

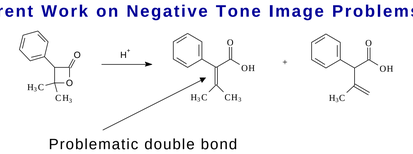
Contact printing at 248 nm

Negative tone image developed with THF

Crosslinking suspected



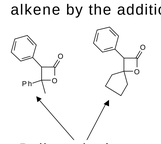
Current Work on Negative Tone Image Problems



Problematic double bond

Polymerization of double bond in ring-opened product is suspected as cause of negative tone image

Solution is to inhibit the polymerization of the alkene by the addition of bulky substituents



Bulky substituents

Efforts are currently under way to synthesize polymers of these compounds for lithographic testing

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