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Designing a non-volatile imaging switch for mass-persistent, chemically amplified photolithography: a model study

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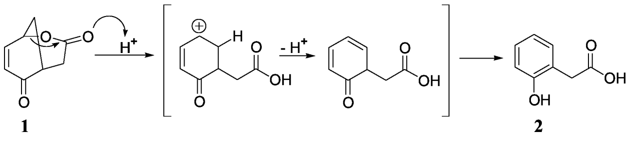
An acid catalysed rearrangement that transforms a bicyclic lactone into a phenolic carboxylic acid has been tested for potential use in chemically amplified microlithographic imaging.

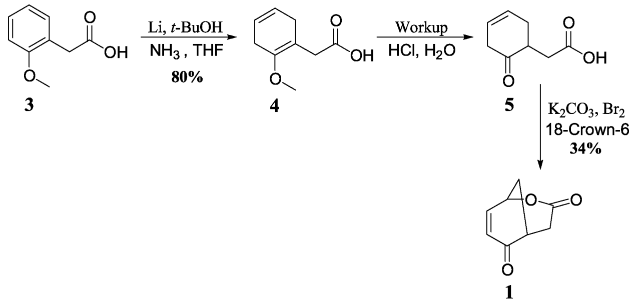
Standard silicon-based microchips are manufactured through an iterative photolithographic process where individual components are transferred into silicon *via* projection through a series of patterned masks. Critical to the success of this technique is a carefully designed polymeric photoresist. Coated on the silicon substrate, the resist undergoes a solubility change only where selectively irradiated and allows pattern transfer from the mask.[1]

In the early 1980's we developed the highly sensitive chemically amplified photolithographic resist system[2] that relies on the entropically favourable release of volatile by-products to provide the driving force for pattern transfer *via* a catalytically activated solubility switch. For example, phenolic polymers containing *tert*-butyloxycarbonyloxy pendant groups or polymers with *tert*-butyl ester groups are selectively unmasked in imagewise fashion by a catalytic amount of a photogenerated acid (PAG) releasing carbon dioxide and/or 2-methylpropene. While chemically amplified resists[3–7] derived from this early invention[2] are used almost universally in the fabrication of microelectronic devices today, the demand for more powerful computers continues to push the limits of this process for the production of ever smaller computer chips.[8] One way to accomplish this reduction is to alter traditional photolithographic techniques to incorporate shorter irradiation wavelengths.[9] However, as exposure tools become more expensive in order to accommodate this shift, damage to the optics by the release of organic volatiles from the resist itself becomes a major issue.[10] To reduce the release of gaseous components, we designed a new solubility switch model employing an enthalpic rather than entropic driving force as shown in Scheme 1. We proposed that, in the presence of a catalytic amount of acid, lactone **1**[8] would be converted to antithetically soluble phenolic acid **2** because of the enthalpically favourable formation of an aromatic ring. Being acid catalysed, the rearrangement would also be compatible with the existing type of PAG's used today with chemically amplified (CA) resists in photolithography.

To test the feasibility of this proposed acid catalysed rearrangement, we synthesized model lactone **1** as shown in Scheme 2. Regioselective Birch reduction of 2-methoxyphenylacetic acid **3** provided exclusively enol ether **4**, which was acidified on workup to give ketoacid[10] **5** in approximately 80% yield. Subsequent bromolactonization followed by *in situ* elimination generated ketoester **1**. It should be noted that various lactonization conditions with sources of both iodine and bromine were attempted. Although this route only provides a fair yield of the desired ketoester **1**, it provided the best results and enabled the production of a substantial amount of product.[11]

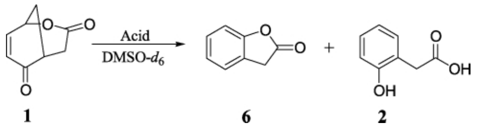


Scheme 1



Scheme 2

Preliminary evaluation of the acid catalysed rearrangement was accomplished by dissolving ketoester **1** in deuterated dimethyl sulfoxide. This choice of solvent allows heating of the solution of **1** to just under its boiling point of 189 °C. Several different acids used in catalytic amount were tested for this reaction and the various solutions were heated with monitoring of reaction progress by NMR spectroscopy.[12] In the cases where the rearrangement occurred, both the desired phenolic acid **2** and some of the corresponding cyclised aromatic lactone by-product **6** were formed (Scheme 3).



Scheme 3

Product distributions for each set of conditions are shown in Table 1. As expected, no measurable conversion of **1** into **2** and/or **6** was observed in the absence of acid catalyst upon heating to a temperature of 185 °C. In the presence of triflic acid the rearrangement takes place with initial formation of phenolic acid **2** as the major product. Prolonged heating increases the

Table 1 Product distributions obtained upon heating ketoester **1** with various acids[a]

Acid	150 °C for 1 min	185 °C for 2 min	185 °C for 15 min
None	**1**	**1**	N/A
HNO_3	**1**	**1**	N/A
$HClO_4$	**1**	7% **2** + 93% **1**	35% **2** + 10% **6** + 55% **1**
CF_3SO_3H	**1**	26% **2** + 8% **6** + 66% **1**	48% **2** + 48% **6** + 4% **1**
PAG[b]	**1**	10% **2** + 90% **1**	25% **2** + 8% **6** + 67% **1**

[a] Product distributions determined by integration of ^1H NMR yielded the relative ratios of compounds **1**, **2**, and **6**. ^1H NMR spectra of compounds **2** and **6** were obtained from the literature.[13] [b] Photoactive acid generator (diphenyl [4-(phenylthio)phenyl] sulfonium hexafluoroantimonate salt).

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relative amount of aromatic lactone **6** that is formed, and, after 15 min, the reaction is almost complete affording an equal mixture of **2** and **6**. While the temperature required for this rearrangement to take place clearly exceeds that used with today's CA resists, the fact that it occurs with triflic acid is encouraging since the counterions of many photogenerated acids are fluorinated sulfonates. In addition, past experience with various generations of commercial CA resists has shown that a reaction affecting only a small number of pendant groups in a CA resist is sufficient to effect the desired solubility switch.[3b] Differential scanning calorimetric measurements suggest that the uncatalysed rearrangement of **1** into **2** takes place near 225 °C with subsequent transformation of **2** into lactone **6** taking place near 250 °C.

Although not yet optimised, ketoester **1** clearly demonstrates that a rearrangement that unmasks both a phenol and a carboxylic acid, affording the solubility switch necessary for chemically amplified photolithography, can, in principle, take place in 'mass persistent' fashion without the concomitant evolution of large amounts of volatile organic material as observed with today's CA resists. In order to implement this chemistry into an actual photoresist, structure **1** would have to be incorporated as a pendant group in a polymer or copolymer used in a chemically amplified formulation[3b] in conjunction with a photoacid generator such as a triarylsulfonium salt. Exposure of a coating of this formulation to radiation would then generate acid within the resist, and a subsequent baking step would accomplish the desired solubility change by transforming the pendant group derived from **1** to one derived from **2** (hence soluble in typical aqueous base developers) in the exposed areas of the coating.

In summary, an organic soluble bicyclic lactone that can undergo acid catalysed rearrangement to unmask moieties soluble in aqueous base without extensive release of volatile organic by-products has been designed and synthesized. This design incorporates the enthalpically favourable formation of an aromatic ring as the driving force rather than the typical entropically favoured release of small molecules arising from removal of a protecting group. Preliminary experiments performed in solution have demonstrated that conversion of the model compound can be achieved with aromatization and change in solubility properties upon heating in the presence of a catalytic amount of acid.

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11. (6-Oxocyclohex-3-en-1-yl)acetic acid (**5**). To 100 mL of condensed ammonia stirring at −55 °C under argon was added a solution of 5.0 g (30 mmol) of 2-methoxyphenylacetic acid and 7.2 mL (75 mmol) of *tert*-butyl alcohol in 20 mL of tetrahydrofuran. Small pieces of 15 cm of Li wire (97 mmol, 45 mg/cm) were added in three portions. The first addition was immediate; the second followed it by one half hour; and the third followed the second by one hour. The blue color persisted only after the third addition. After the mixture had stirred overnight, methanol was slowly added to discharge the remaining blue color. The mixture was warmed to room temperature and 200 mL of 1N aqueous HCl was added. This addition was followed by dropwise addition of concentrated HCl until a pH of 0 was measured. The solution was stirred at pH 0 for one minute and then raised to pH 4 with slow addition of a 1M aqueous NaOH solution. The aqueous layer was immediately extracted with Et_2O (2 × 200 mL). The combined organic layers were washed with brine (1 × 100 mL), dried over $MgSO_4$, and filtered. The solvent was removed *in vacuo* to yield 3.67 g (79%) of acid **5**.
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13. 2-Oxabicyclo[3.3.1]non-7-ene-3,6-dione (**1**). To a solution of 10.0 g (52 mmol) of acid **5** and 1.37 g (5.2 mmol) of 18-crown-6 ether in 260 mL of dry CH_2Cl_2 stirring at 0 °C under N_2 was added 14.3 g (104 mmol) of potassium carbonate followed by 3.5 mL (67 mmol) of Br_2 dropwise. After the mixture had warmed to room temperature overnight, 200 mL of water was added. Extraction of the crude material with CH_2Cl_2 (2 × 200 mL), evaporation of the solvent and chromatography of the resulting oil in 3:2 ethyl acetate/hexanes yielded 2.68 g (34%) of ester **1** as a white solid.