Journal of the American Chemical Society

1989

Formation of Monolayer Films by the Spontaneous Assembly of Organic Thiols from Solution onto Gold

- From solution, a wide variety of long chain alkanethiols absorb onto gold surfaces to form well ordered surface monolayers
- “Soft” nucleophiles such as sulfur interact well with the gold surface
- Whereas, “hard” acids and bases have very low reactivity with the gold surface
- Both very hydrophobic and very hydrophilic surfaces can be created by this technique – contact angles

p. 321-335

MM3 Force Field for Hydrocarbons

- Improvement over early and later versions of the MM2 force field as a result of an increase in experimental data
  - Now able to simultaneously predict vibrational frequencies, structures, and heats of formation
  - Problems that are “corrected” in this version by adding more terms
    - Underestimation of high C-C bond rotational barriers in congested hydrocarbons
    - Close H/H nonbonded repulsions are too large for small distances (under 2A)
    - Bonds which are eclipsed are too short (ex. Ethane)
    - Problems with charge treatment in aromatic systems
    - Bending function doesn’t adequately account for large deformations

p. 8551

MM3 Force Field for Hydrocarbons

- Bond stretching

$$E_s = 71.94k_s(l - l_0)^2[1 - 2.55(l - l_0) + (7/12)2.55(l - l_0)^2]$$

- Angle bending

$$E_\theta = 0.021914(k_\theta)(\theta - \theta_0)^2[1 - 0.014(\theta - \theta_0) + 5.6(10^{-5}) \times (\theta - \theta_0)^2 - 7.0(10^{-7})(\theta - \theta_0)^3 + 9.0(10^{-10})(\theta - \theta_0)^4]$$

- Torsion

$$E_\omega = (V_1/2)(1 + \cos\omega) + (V_2/2)(1 - \cos 2\omega) + (V_3/2)(1 + \cos 3\omega)$$

- Stretch-bend interaction
- ….and many other interactions (van der Waals, etc.)

If a simple theory doesn't work quite right just make it more complicated and add more terms to the equations

An Internal Coordinate Monte Carlo Method for Searching Conformational Space

- The multiple-minimum energy problem is the main concern of this paper
- In searching conformational space, changes in torsion angle are more important than changes in bond lengths and bond angles as both are rigidly defined by steep potentials (reduction of 3N-6 dimensional space to N dimensional space)
- Use of internal coordinate systems instead of external coordinate systems simplify the problem somewhat
- Dividing a large molecule up into appropriate smaller molecules is also imperative to reduce the complexity of the problem

p. 4379-4386

Major results from this paper

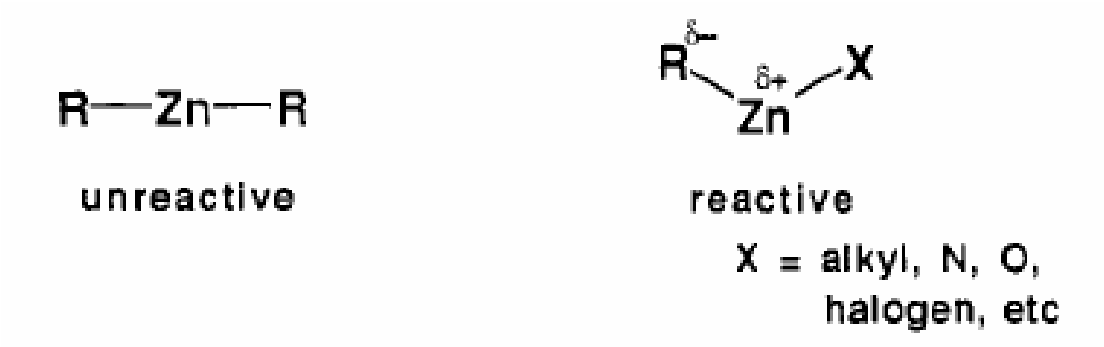
- Uniform usage of stored structures as starting geometries led to improvements
- Varying number of torsional rotations in each MC step also led to improvements
- Low-energy conformers are typically more related than high-energy conformers

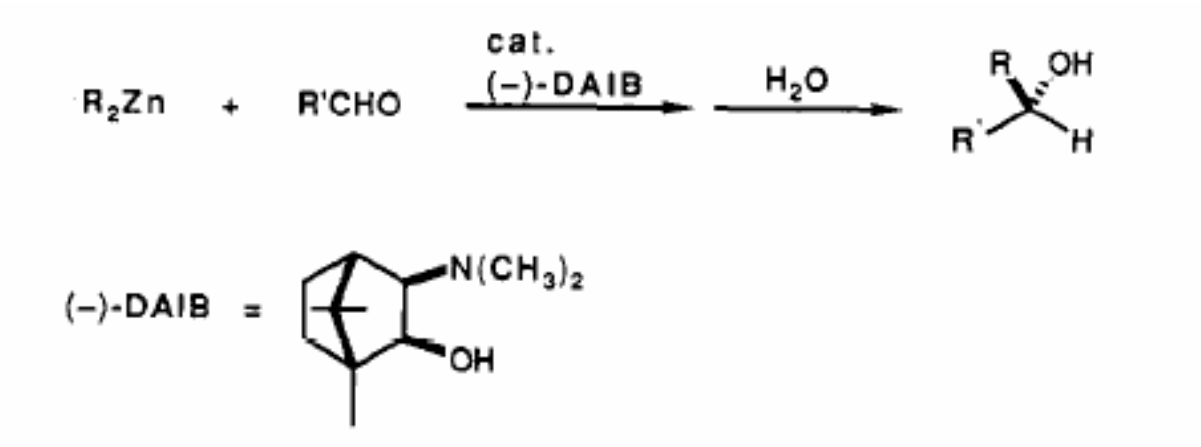
Reactions of Carbonyl Compounds with Grignard Reagents in the Presence of Cerium Chloride

- Adding $CeCl_3$ to a THF solution minimizes
  - 1,4 addition
  - enolization for easily enolizable ketones (reduces potential side products)
- $CeCl_3$ is very oxophilic and as a result increases the reactivity of the oxygen

p. 4392

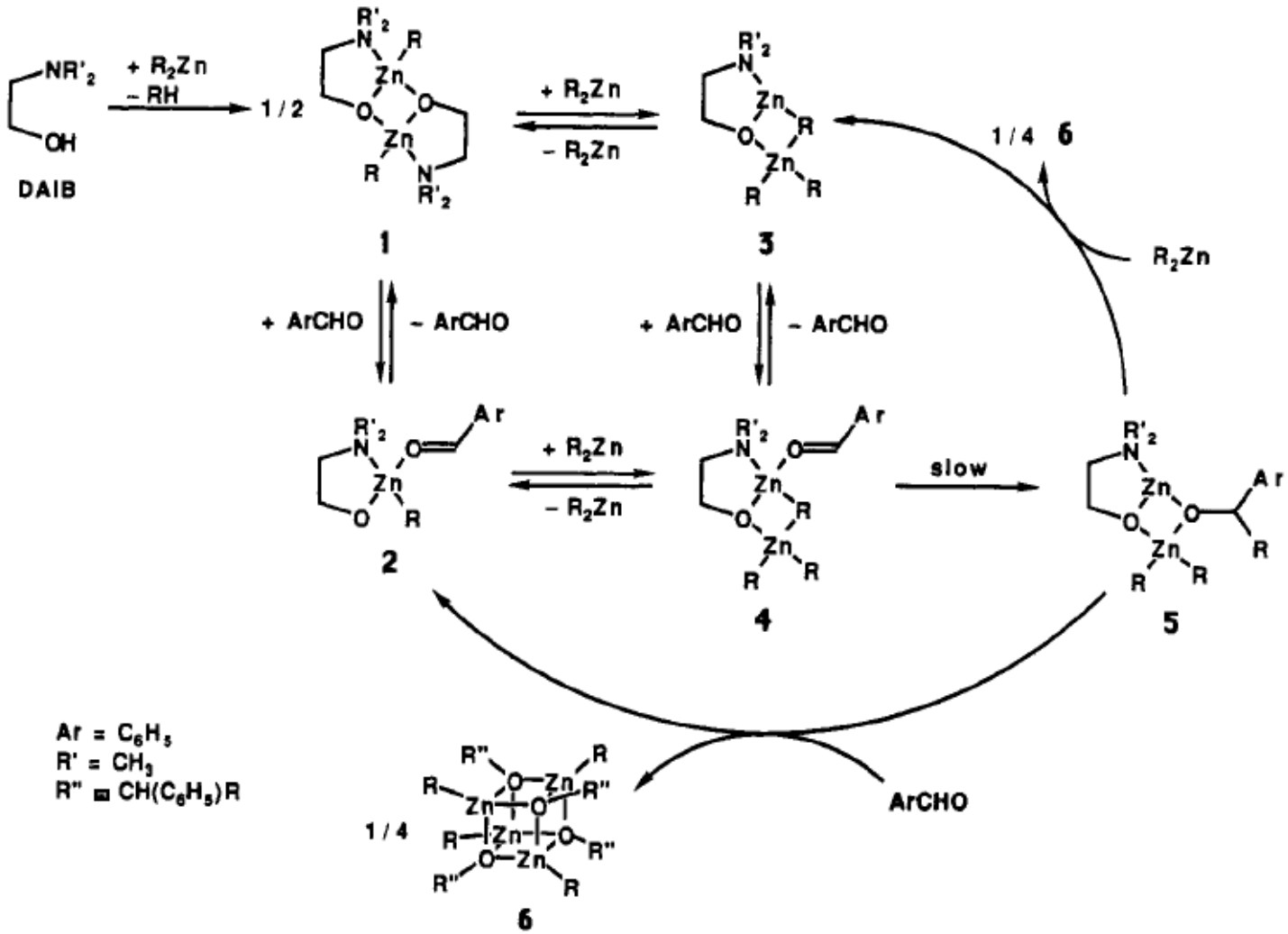
Enantioselective Addition of Dialkylzincs to Aldehydes Promoted by Chiral Amino Alcohols. Mechanism and Nonlinear Effect





p. 4028

Mechanism


DAIB
+ R2Zn
– RH
1 / 2
1
+ R2Zn
– R2Zn
3
1 / 4 6
R2Zn
+ ArCHO
– ArCHO
+ ArCHO
– ArCHO
2
+ R2Zn
– R2Zn
4
slow
5
Ar = C6H5
R' = CH3
R" = CH(C6H5)R
1 / 4
6
ArCHO

Nonlinear Effect

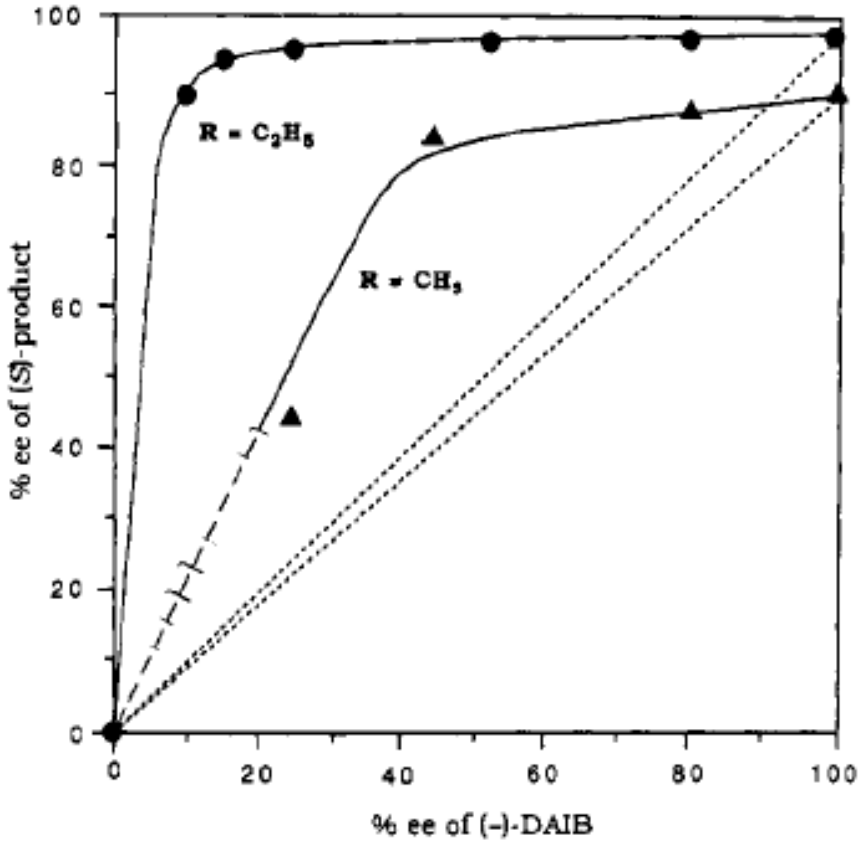
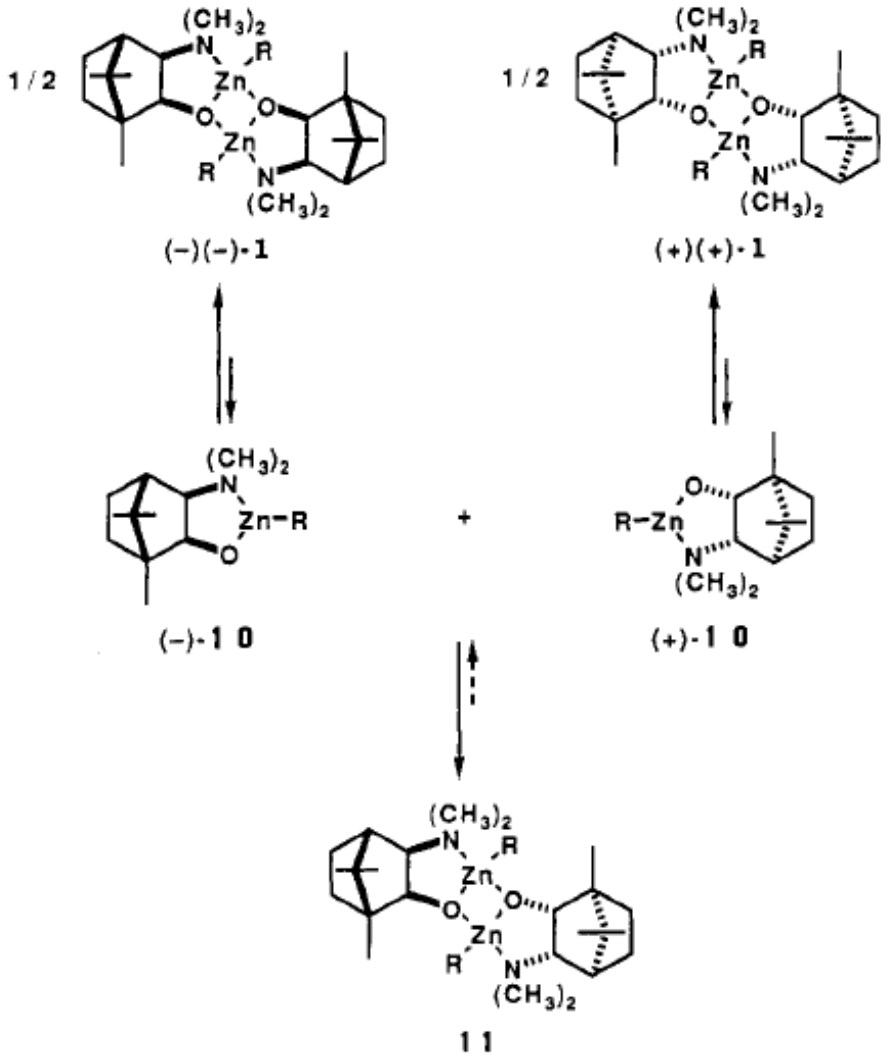
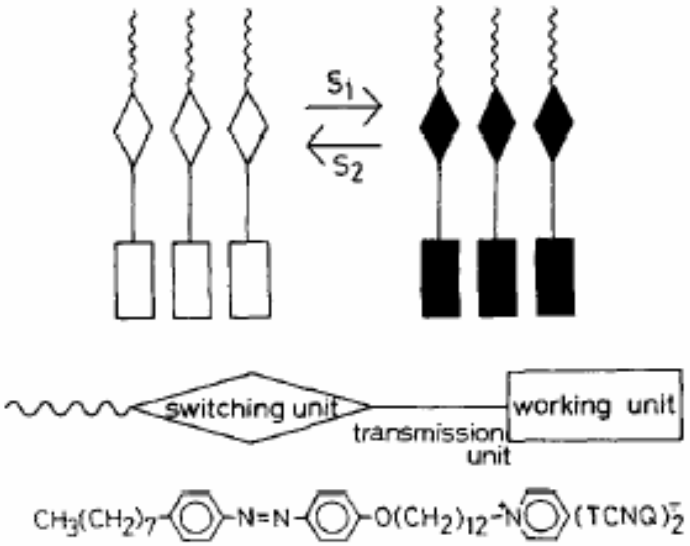


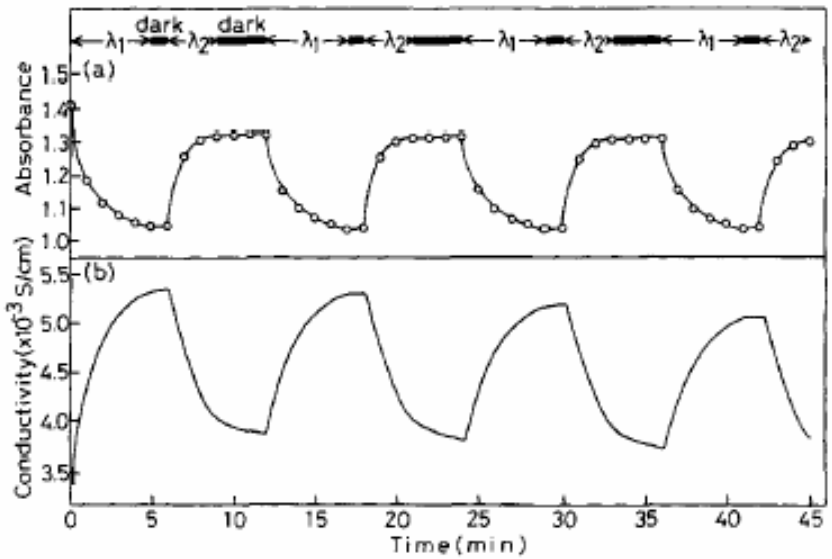
Figure 2. Correlation between the ee of the alkylation product and the ee of the chiral auxiliary: (●) Reaction using 0.42 M $(C_2H_5)_2Zn$, 0.42 M C_6H_5CHO, and 34 mM (−)-DAIB in toluene at 0 °C; (▲) 0.47 M $(CH_3)_2Zn$, 0.49 M C_6H_5CHO, 47 mM (−)-DAIB in toluene-d_8 at 32 °C.

Explanation



Photochemical Switching in Langmuir-Blodgett Films p.3080





Direct Polymerization of Acetylene to Give Living Polyenes

- First example of living polymerization of acetylene itself
- Long conjugated system lends itself to being a potential organic conductor
- W-(CH-t-Bu)(NAr)(O-t-Bu)$_2$ (Ar = 2,6-C_6H_3-i-Pr_2)
  - Longer chains are intractable and black
  - Shorter chains are colored from yellow to orange
- Block copolymers with norbornene to demonstrate the living polymerization

p. 8004