**The Cannizarro Reaction: Lab Experiment #10**

**An example of a base driven attack on carbonyls *lacking* an `alpha’ H**

***The hydride anion (H-) transfer reaction***

**(see also: McMurry pp 599-600)**

The reactivity of carbonyl compounds to base attack is mainly connected to the unusual acidity of the `alpha’ (α) H. For example, the aldol condensation last week, which resulted in the tan, `baby spit up’ product , dibenzalacetone started with attack on OH- on the α- H to form water and a carbanion as shown below

α- H sites carbanion





+ OH- + H2O

But what if the carbonyl does not have any α- H sites? Under certain circumstances, notably when a rich supply of electrons resides in the initial substrate, a second class of reaction can occur featuring an unusual species: **H-, the hydride anion.1**

In the present reaction run over the last week just such a shift was taken advantage of to produce the following overall reaction:



**1**

 1 NaOH 2 benzaldehydes benzyl alcohol sodium benzoate

 (reduced) (oxidized)

 Soluble in CH2Cl2 soluble in water

The simultaneous conversion of aldehyde to both oxidized and reduced forms is referred to as a disproportionation.

The mechanism, proposed by Swain et. al. **J. Amer. Chem Soc.** ,**101**, 3576 (1979), goes something like this:

step

Lone pair from O

Forms sigma bond to C



(1) initial OH- attack



Lone pair from O of second OH- forms sigma bond to H and makes H2O



(2)

 Secondary OH- attack

(the benzyl site is electron rich due to nearby phenyl π electrons which stabilizes dianion )

Hydride anion ejection and attack



(3) (-δ)

 Exchange can be thought of in terms of separate H- generation

Lone pair responds to loss of C’s bond by forming π bond to that C

 (-) charge transfer



 (-δ)



 **H** - +

(3a)

C-H bond breaks and both electrons go to H

Followed by H- attack on second benzaldehyde

H- donates both electrons to form bond with carbonyl C and π bond of carbonyl breaks and transfers both electrons to O forming a lone pair and making O negative



(3b)

The benzyl alcohol anion is highly basic and thus abstracts an H from H2O to regenerate an OH- , making the net OH- consumption 1 mole of OH- for two moles of benzaldehyde reactant.

The corresponding carboxyl anion formed from the original dianion in (2) is charge neutralized by the Na+ from the NaOH, thus producing the net products in **1** above.

1 for further reading see for example, Carey and Sundberg, ***Advanced Organic Chemistry Part***

***B: Reactions and Synthesis*** *pp 218-220 2nd edition 1983.* The Cannizzaro reaction mimics many biological reactions wherein carbonyl reductions occur. For example: NadH🡪 Nad+ + H- and the generated H- reduces carbonyls in a variety of metabolic processes in the body. It is noted that most organic reactions find alternative routes to reduction, a difference that sets apart the biological from the purely chemical worlds.