

# The Chemistry of Carboxylic Acids

## April 19, 2013

- Quiz #1 results, score distributions, and planning for the future.
- Preparation and use of anhydrides.
- Reduction of acids, esters, and acid chlorides.
- Ester vs. amide hydrolyses.

### Announcements

**Quiz #1 Results:** Mean = 15.4/30 pts, Standard Deviation = 6.2, High = 29.

**Suggested Problems for Chapter 20:** 20.25, 20.27, 20.30, 20.32, 20.35, 20.38, 20.40, 20.43, 20.45, 20.46, 20.49, 20.51, 20.53, 20.55. Chapter 21: 21.31, 21.34, 21.35, 21.39, 21.43, 21.44, 21.46, 21.48, 21.51, 21.53, 21.54 (b,d), 21.55 (f,g,h,i), 21.56 (b,c,e), 21.60.

**TA Office Hours:** Mon 7-8 pm: Rob Craig - 302 Schlinger (x4056); Tue 3-4 pm: Kelly Kim - 302 Schlinger (x4047); Tue 7-8 pm: Corey Reeves - 302 Schlinger (x4056); Wed 5-6 pm: Adam Boynton - 139 Noyes (x3202); Wed 8-9 pm: Ben Suslick (UTA) - Lloyd Lounge; Thu 8-9 pm: Evan Zhao (UTA) - Fleming Lounge ; Thu 9-10 pm: Crystal Chu - 202 Schlinger (x3634); Sun 3-4 pm: Chung Wan Lee - 302 Schlinger (x4056).

**Mechanism Workshop:** 153 Noyes from 9-10 PM on Sunday, April 21.

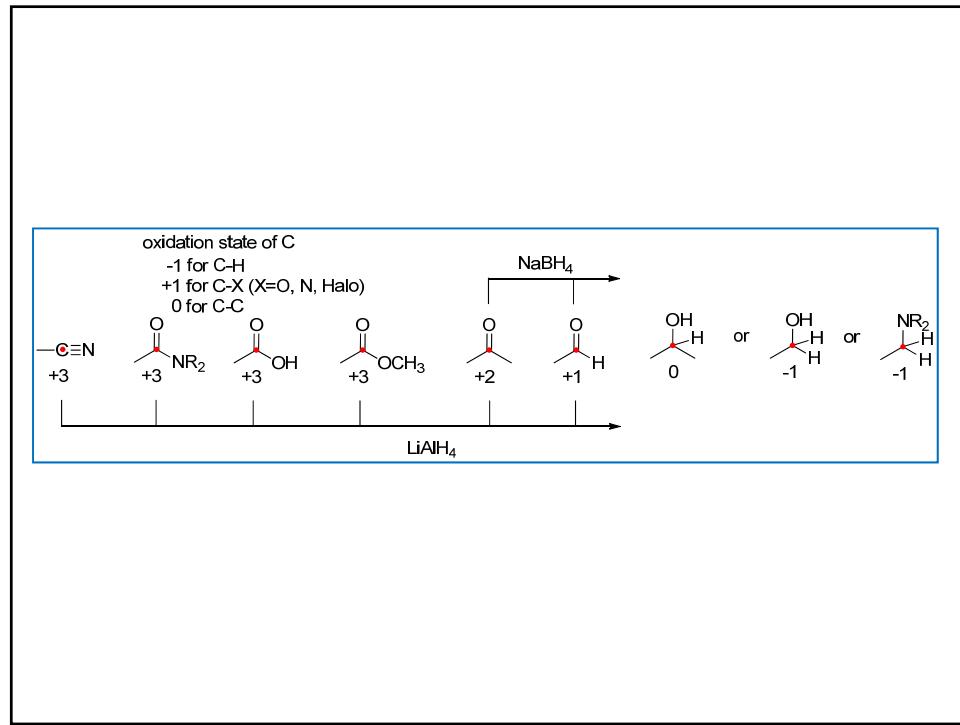
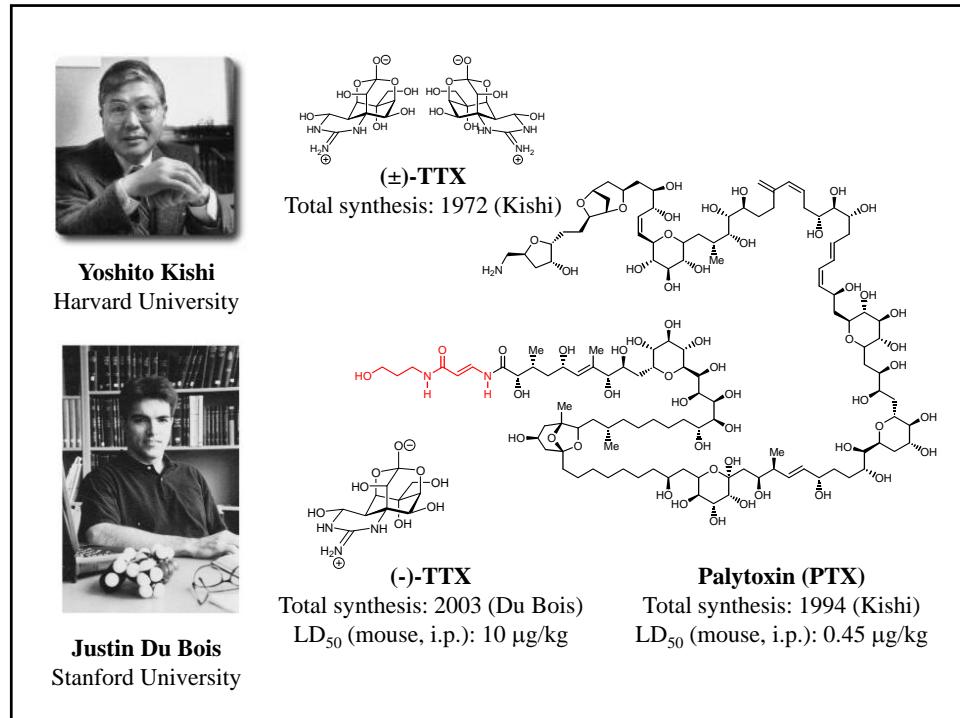


Table 1. Relative toxicities of a selected group of toxic substances.

Toxin	Minimum lethal dose ( $\mu\text{g/kg}$ ) <sup>*</sup>	Source	Form and/or structure	Molecular weight	Reference
Botulinus toxin A	0.00003	Bacterium: <i>Clostridium botulinum</i>	Protein Crystalline, A	900,000	(61)
Tetanus toxin	.0001	Bacterium: <i>Clostridium tetani</i>	Crystalline	100,000	(61)
Ricin	.02	Plant: castor bean, <i>Ricinus communis</i>	Nonprotein (62)		
Diphtheria toxin	.3	Bacterium: <i>Corynebacterium diphtheriae</i>		72,000	
Cobra neurotoxin	.3	Snake: <i>Naja naja</i>			(62)
Crotalus toxin	.2	Snake: rattlesnake, <i>Crotalus atrox</i>			(62)
Kokoi venom	2.7†	Frog: <i>Phrynobatrachus bicolor</i>	Nonprotein	~400	(11)
Tarichatoxin	8	Newt: <i>Taricha torosa</i>	(C <sub>11</sub> H <sub>17</sub> N <sub>2</sub> O <sub>4</sub> )	319	(12)
Tetrodotoxin	8-20	Fish: <i>Tetraodon rubripes</i>	(C <sub>11</sub> H <sub>17</sub> N <sub>2</sub> O <sub>4</sub> )	319	(9, 10)
Saxitoxin	9	Shellfish. Produced by dinoflagellate <i>Gonyaulax catenella</i> ingested by shellfish	(C <sub>10</sub> H <sub>17</sub> N <sub>2</sub> O <sub>4</sub> · 2HCl)	372	(9)
Bufoxin	390	Toad: <i>Bufo vulgaris</i>	Vulgarobufotoxin (C <sub>18</sub> H <sub>30</sub> N <sub>2</sub> O <sub>10</sub> )	757	(62)
Curare	500	Plant: <i>Chondodendron tomentosum</i>	d-Tubocurarine (C <sub>28</sub> H <sub>44</sub> N <sub>2</sub> O <sub>12</sub> )	696	(62)
Strychnine	500	Plant: <i>Strychnos nux-vomica</i>	(C <sub>21</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub> )	334	(62)
Muscarin	1,100	Mushroom: <i>Amanita muscaria</i>	(C <sub>18</sub> H <sub>30</sub> O <sub>2</sub> Cl)	210	
Samandarin	1,500	Salamander: <i>Salamandra maculosa</i>	(C <sub>18</sub> H <sub>30</sub> O <sub>2</sub> N)	397	(33)
Disopropyl-fluorophosphate	3,000		Synthetic nerve gas [(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> P(O <sub>2</sub> F) <sub>2</sub> ]	184	
Sodium cyanide	10,000		Synthetic NaCN	49	(62)

\* Minimum lethal dose refers to mouse except in the case of ricin, where it refers to guinea pig (see 61), and of bufoxin and muscarin, where it refers to cat. In cat, administration was intravenous; in all other cases it was intraperitoneal. Since the survival times are not always specified and the experiments are not direct comparisons, these values are of necessity approximate and indicative only of relative toxicity by the indicated route of administration. † LD<sub>50</sub> in mouse, administered intravenously.

Mosher, et al. *Science*, 1964, 144, 1100.

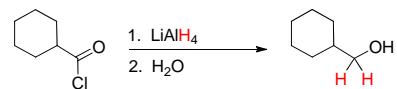


## Reduction of Acid Chlorides with $\text{LiAlH}_4$ and $\text{LiAlH}(\text{O}t\text{-Bu})_3$

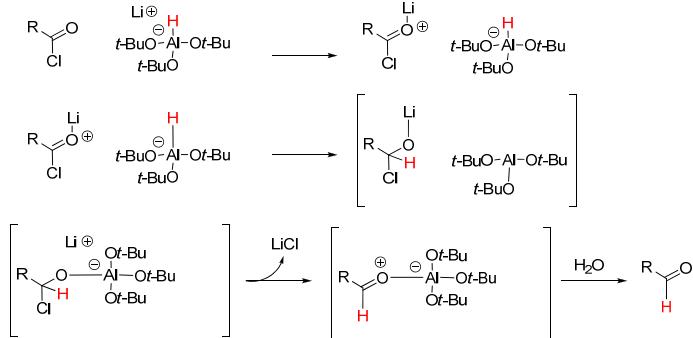
Lithium tri-*tert*-butoxyaluminum hydride reduction:



Lithium aluminum hydride gives the alcohol:

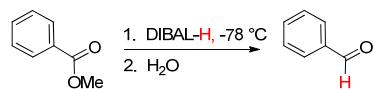


### Mechanism:

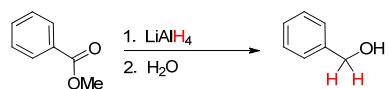


## Reduction of Esters with $\text{LiAlH}_4$ and DIBAL-H

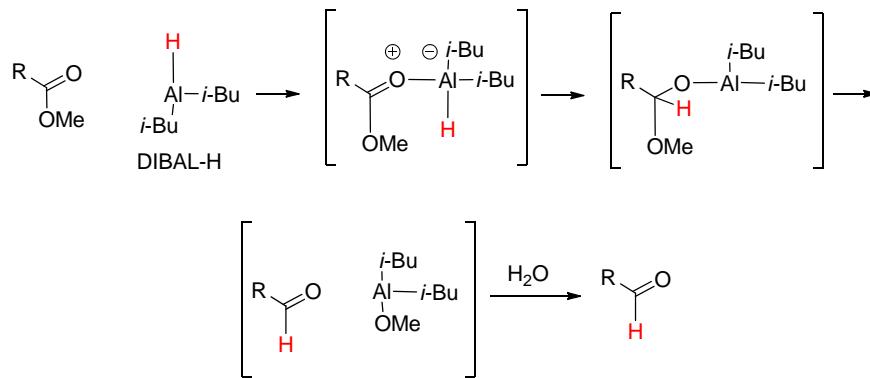
Diisobutylaluminum hydride (DIBAL-H) gives the aldehyde:



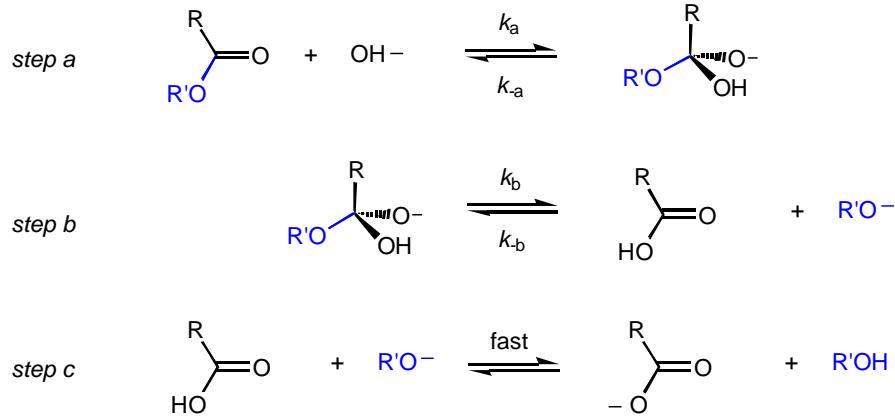
Lithium aluminum hydride gives the alcohol:



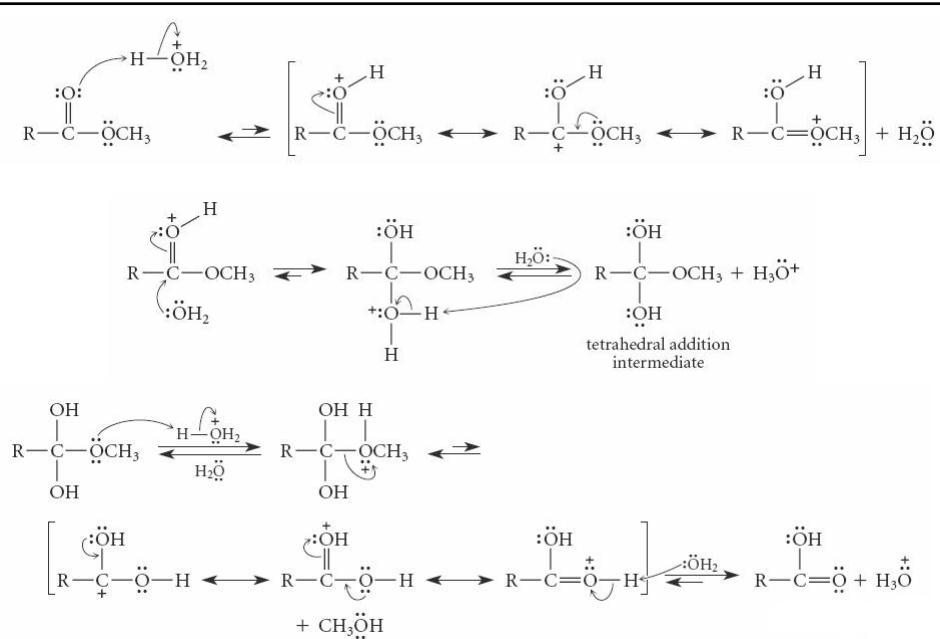
### DIBAL Mechanism:



## Base-Promoted Hydrolysis of Esters

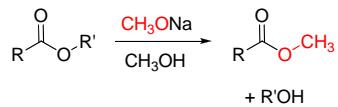


If RO- is a better leaving group than HO-, then the  $k_b$  step is fast,  $k_a$  is rate determining.

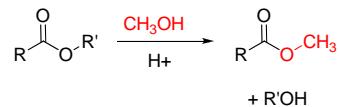


## Transesterification & Biodiesel Production

*Base-promoted transesterification:*



*Acid-Catalyzed transesterification:*



The mechanism for these processes is identical to the base-promoted and acid-catalyzed hydrolysis reactions!

*Application in biodiesel production:*

