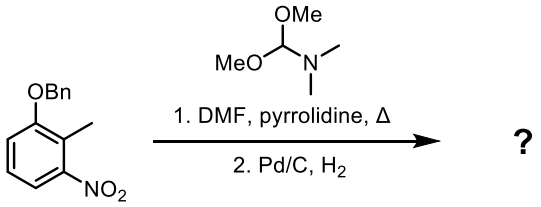
E. Anderson Group – Problem Set 12/10/21 (Pavle & Ryan)

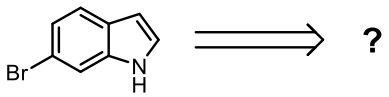
Pavle

Revision:

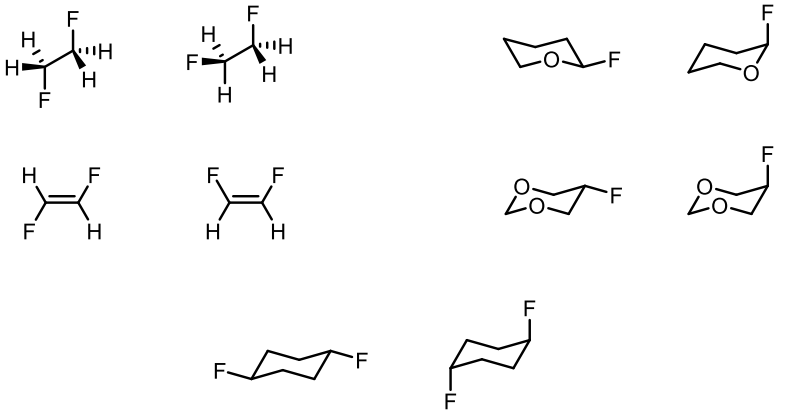
a) Provide the product of Leimgruber–Batcho reaction.



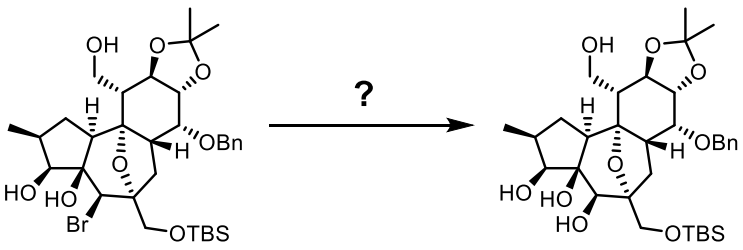
b) You wanted to buy 6-bromoindole (190 £/g), but your supervisor disapproved your order. Can you come up with a way to make it from much cheaper starting material?



c) Select the more stable structure in each of the pairs.

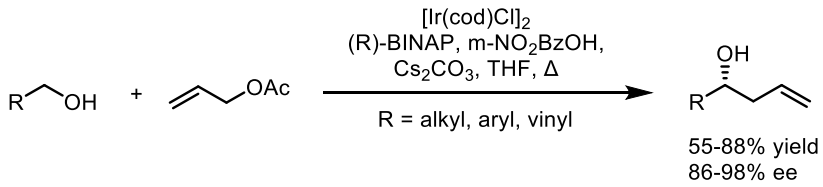


d) Provide a two-step sequence to solve the following tactical problem from Wender's total synthesis of daphnane diterpenes.

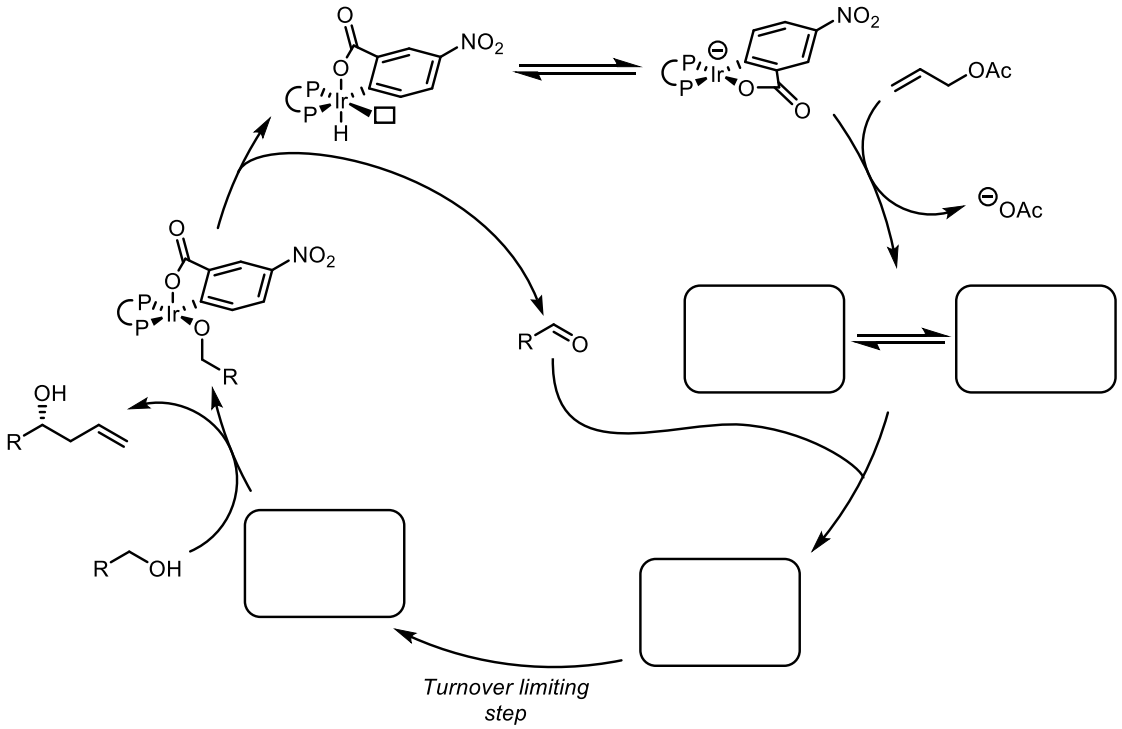


Progression:

1. In 2008 Krische group published their seminal work on catalytic enantioselective carbonyl allylation.



a) Fill in the boxes

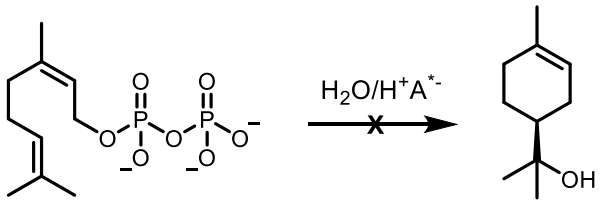


b) Why is 3-nitrobenzoic acid working better in this reaction than benzoic acid?

As both substrate and product are primary alcohols, is there a possibility for further reactions of the product to produce oligomers?

Ryan, Problem set, 12/10/21

With the recent Nobel you were inspired to make α-terpineol *via* a semi-biosynthetic route to promote green/metal free chemistry! Sadly, as chemistry goes it didn't work... However, you're a diligent chemist and have isolated your major by-product.



Below is the ^{1}H and ^{13}C NMR data for your mystery compound. Figure out what the compound is and draw a mechanism for its formation.

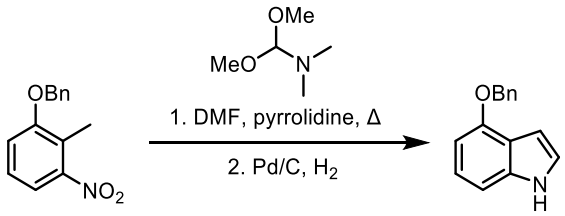
HRMS (ESI^{+}) calc. for $C_{10}H_{16}$ $[M+H]^{+}$ 137.13, found 137.13; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ 4.57 (d, *J* = 1.6 Hz, 1H), 4.50 (d, *J* = 1.6 Hz, 1H), 2.45 - 2.32 (m, 2H), 2.05 – 1.75 (m, 6H), 0.98 (s, 3H) 0.92 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*): δ 149.8, 108.1, 52.8, 40.8, 40.4, 25.9, 25.3, 25.1, 23.7, 23.7

Terry's Chocolate Orange™ to the team that figures out the minor by-product.

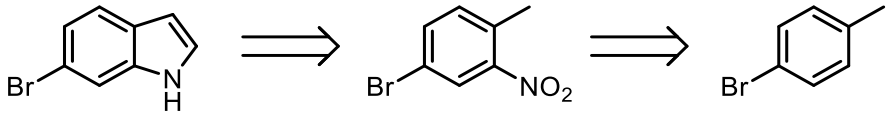
HRMS (ESI^{+}) calc. for $C_{10}H_{16}$ $[M+H]^{+}$ 137.13, found 137.13; **^{1}H NMR** (600 MHz, Chloroform-*d*): δ 4.57 (m, 1H), 2.33 (m, 1H), 2.05 – 1.83 (m, 4H), 1.71 – 1.68 (m, 1H), 1.66 (s, 3H), 0.98 (s, 3H) 0.92 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*): δ 144.4, 116.3, 47.4, 41.2, 37.7, 31.3, 30.3, 25.2, 25.2, 21.2

Pavle, Answers

a)



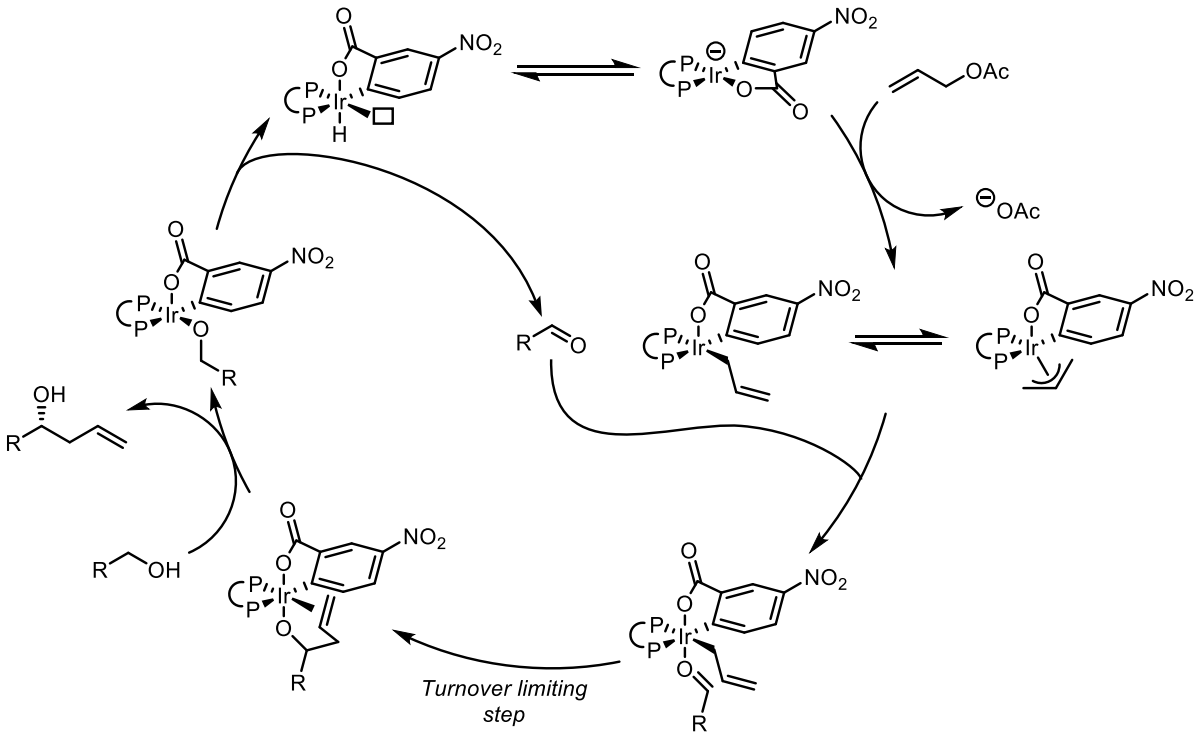
b)



c) Second structure in all cases (anomeric effect).

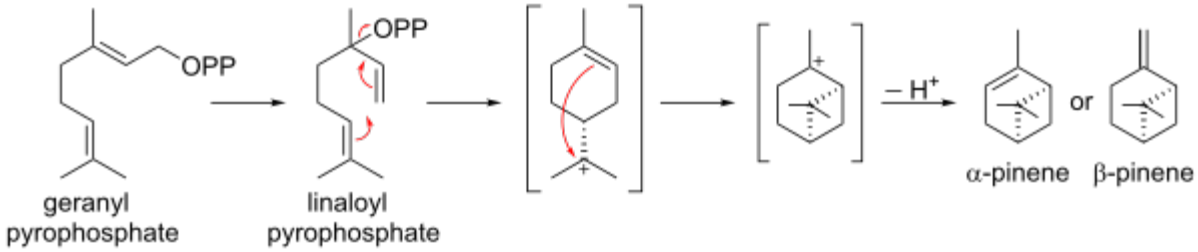
d) i) Zn, NH_4Cl, EtOH; ii) vanadyl acetylacetonate, t-BuOOH, CH_2Cl_2

1. a)



Ryan, Answers

Sadly, your synthesis of α-terpineol failed…



Although you did manage to get 76% and 94% e.e. of β-pine. So, you isomerise it to α-pine and remarket it as a synthesis of these two compounds. Congrats on the JOC/E. Joc. Chem.