

Problem session. January 2015.

1. A pacific sponge contains 2.8% dry weight of a sweet-smelling oil with the following spectroscopic details:

Mass spectrum gives formula $C_9H_{16}O$

IR: 1680, 1635 cm^{-1}

1H RMN δ 0.90 (6H, d, $J = 7$), 1.00 (3H, t, $J = 7$), 1.77 (1H, m), 2.09 (2H, t, $J = 7$), 2.49 (2H, q, $J = 7$), 5.99 (1H, d, $J = 16$), and 6.71 (1H, dt, $J = 16, 7$).

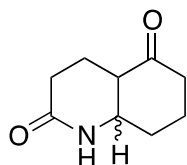
^{13}C RMN δ 8.15 (CH_3), 22.5 (CH_3), 28.3 (CH), 33.1 (CH_2), 42.0 (CH_2), 131.8 (CH), 191.6 (C)

What is the structure?

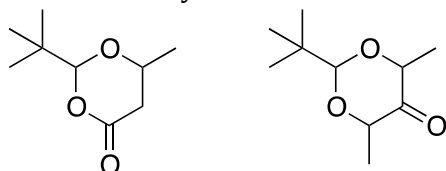
2. Reaction between *tert*-butylaldehyde and *tert*-butylmethylketone in base gives a compound A (1H NMR δ 1.10 (9H, s), 1.17 (9H, s), 6.4 (1H, d, $J = 15$) and 7.0 (1H d, $J = 15$)). When A reacts with HBr gives compound B (1H NMR δ 1.08 (9H, s), 1.13 (9H, s), 2.71 (1H, dd, $J = 1.9, 17.7$), 3.25 (dd, $J = 10.0, 17.7$), 4.38 (1H, dd, $J = 1.9, 17.7$)).

Propose mechanisms and structures and assign the spectra.

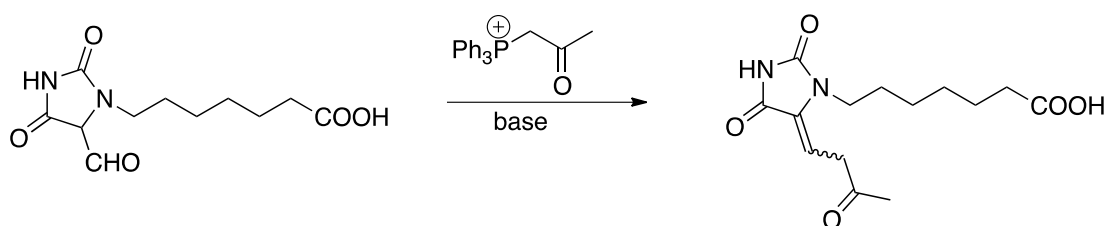
3. Two diastereoisomer of this cyclic keto-lactam have been prepared. The NMR spectra have many overlapping signals but the marked proton can be differentiated. In isomer A it is a quartet with a coupling constant of 3.5 Hz while in B is a double triplet with coupling constants of 4 and 11 Hz. Which isomer has which stereochemistry?



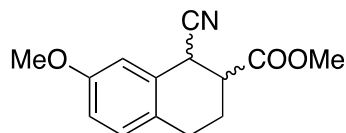
4. How would you determine the stereochemistry of these compounds?



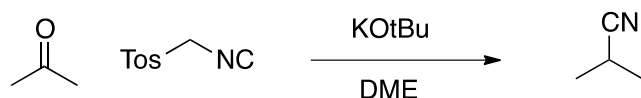
5. The structure of a Wittig product intended as a prostaglandin model was established by the usual methods _ except for the geometry of the double bond. Irradiation of a signal at 3.54 ppm (2H, t, $J = 7.5$) led to an enhancement of another signal at 5.72 ppm, (1H, t, $J = 7.1$) but not to a signal at 3.93 ppm (2H, d, $J = 7.1$). What is the stereochemistry of the alkene? How is it formed?



6. A chemical reaction produces two diastereoisomers of the product. Isomer A has a double triplet at 3.08 ppm ($J = 4, 9.9$ Hz) and a doublet at 4.32 ppm ($J = 9$ Hz). Isomer B has a doublet at 4.27 ppm ($J = 4$). The other protons overlap. Which is the stereochemistry of A and B? How would you transform B into A?

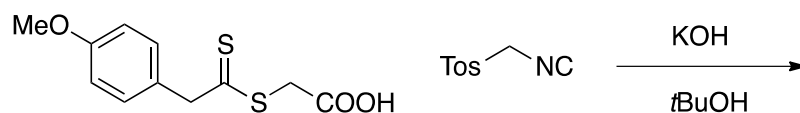
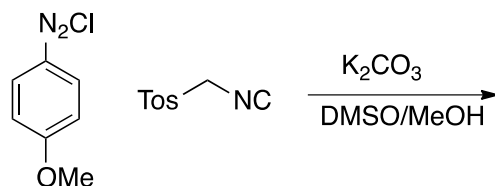
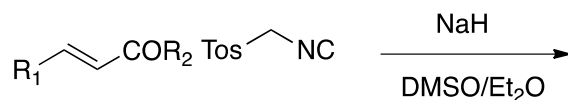
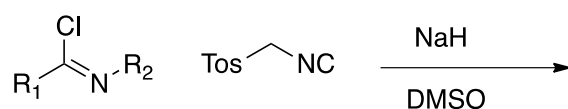
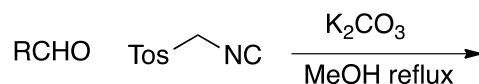
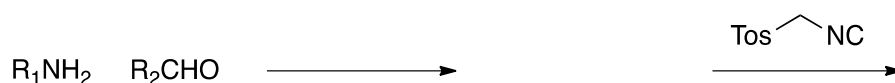


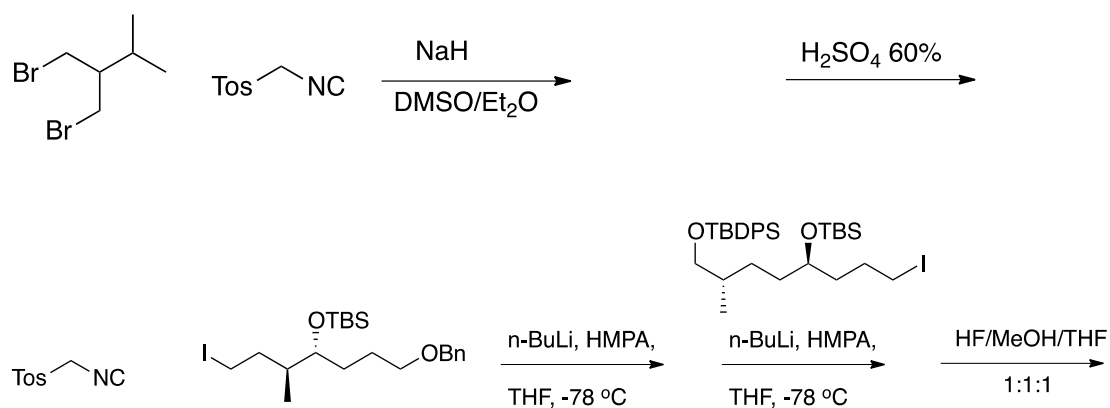
7. Which is the name and the mechanism of this reaction?



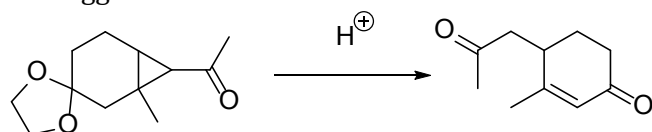
8. If the previous reaction is carried out in ethanol or methanol we obtain a completely different product. What is this product? What is the reason for the change in the reactivity?

9. In fact TosMIC is a very versatile reagent.

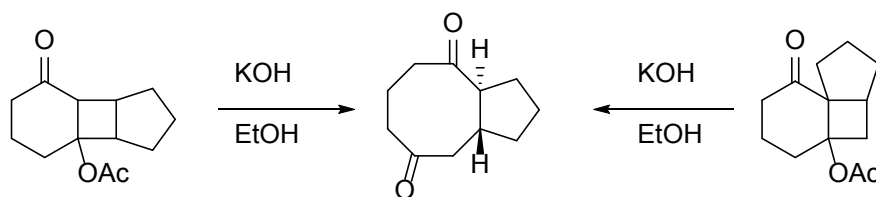




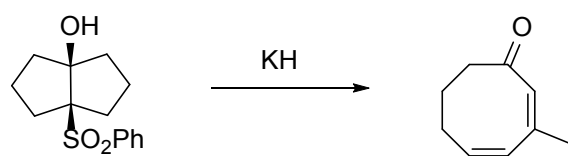
10. Suggest a mechanism for the next transformation



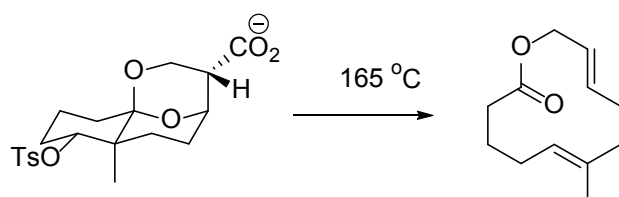
11. Explain why both of these tricyclic ketones fragment to the same diastereoisomer of the same cyclo-octadione.



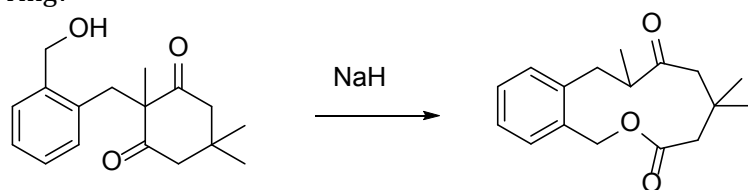
12. Suggest a mechanism for the same reaction.



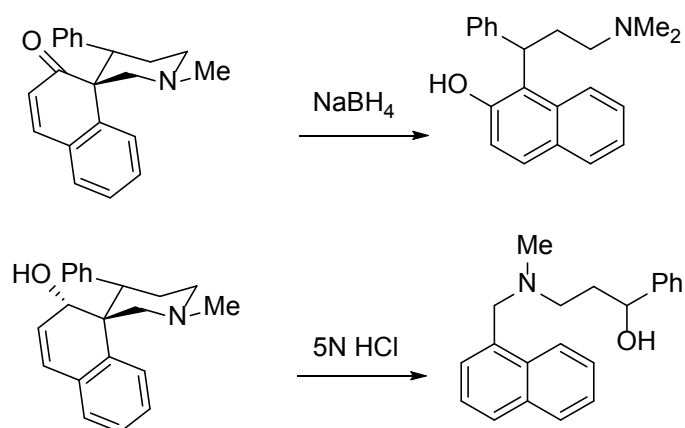
13. Suggest a mechanism for this fragmentation and explain the stereochemistry of the double bonds in the product.



14. Why is this molecule prepared to abandon a stable six-membered ring for a larger ring?



15. These related spirocyclic compounds give different naphthalenes when treated with sodium borohydride or with 5M HCl. Each reaction starts with a different fragmentation. Give mechanisms for the reaction and explain why the fragmentations are different. Treatment of the starting ketone with LiAlH₄ instead of NaBH₄ gives the alcohol below without fragmentation. What's the difference?



16. Suggest mechanism for these reactions explaining the stereochemistry.

