

Questions "Organometals (non-late transition)"

1. Sort by increasing electronegativity: B, Li, Mg, Zn. How is the resulting order reflected by the reactivity of the organometal compounds?
2. How would you prepare methyllithium? Please give the stoichiometrically correct equation.
3. Which structures does methyllithium obtain in THF and benzene solution, respectively? Draw them.
4. Why is *n*-butyllithium less stable than methyllithium? Draw a few products that form from *n*-BuLi at higher temperatures.
5. In the ¹³C NMR spectrum of *i*-Pr⁶Li in THF-*d*₈, two species are observed at 165 K. Which? Explain the shape of the signals.
6. Is it thermodynamically favorable to deprotonate benzene with *n*-BuLi? Which effect would the addition of TMEDA (structure?) have?
7. Why may the Schlosser base be more reactive than even *t*-BuLi? Search for an application in the literature.
8. Chemistry with organolithium compounds requires carefully dried solvents. Sometimes, dry THF is kept dry by boiling it with potassium metal (be careful!). As indicator, benzophenone is added. How does this work?
9. Give an example of a color indicator that allows the titration of *n*-BuLi solutions.
10. Why isn't it advised to store solutions of *n*-BuLi in THF? What happens and why?
11. What happens if benzylpropargylether is treated first with *n*-BuLi and then with (*S*)-propenoxide? Could LDA (structure?) be used here instead of *n*-BuLi? Is LDA an organolithium compound?
12. What happens if benzylprenylether is treated with *n*-BuLi? Which reaction class is concerned?
13. Organolithium reagents can be formed *in situ* from organotin reagents. How?
14. What happens if DMAS-protected imidazole is treated first with *n*-BuLi (1 equiv.) and then with TBSCl?
15. Achiral alkylcarbamates can be lithiated enantioselectively. Give an example. Structure of (-)-sparteine? What can one do with the metalated product?
16. Why may it be interesting to deprotonate ferrocene carboxamide with *n*-BuLi/(-)-sparteine? Quench it with Ph₂PCl.
17. Halogen/lithium exchange proceeds rapidly with *t*-BuLi. How many equivalents are necessary and why?
18. Below which temperature do you expect configurationally stable, acyclic alkylolithium compounds? Inversion barrier of CH₃⁻ vs. NH₃? Are lithiated cyclopropane derivatives more or less stable (estimated inversion barrier)? How do sulfones behave?

19. How would you synthesize ethyl (*S*)-2-methylbutyrate starting from (*R*)-2-butanol? Does iodine/lithium exchange proceed via inversion or retention?
20. Mechanism of the formation of EtMgBr from Mg and EtBr? What is Rieke-Mg?
21. You may have heard of the Schlenk equilibrium of (not only) organomagnesium compounds. Temperature-dependence? Propose an NMR experiment.
22. An advanced reagent is (TMP)MgCl-LiCl (TMP = 2,2,6,6-tetramethylpiperidin-1-yl, Hauser base). Structure? Role of LiCl?
23. Propose the conversion of methyl *p*-iodobenzoate to a benzhydryl alcohol via I/Mg exchange.
24. Conversion of *p*-iodoanisole to *p*-methoxyphenylglycine?
25. What happens if 2,4-dibromoanisole is first treated with *i*-PrMgCl and then with CO₂? Why is rather elevated temperature (40 °C) required for the initial magnesiation?
26. Which preferred diastereomer do you expect on reaction of EtMgBr with (*R*)-2-benzyloxybutanal? Why?
27. Addition of organomagnesium to carbonyl compounds is also possible under enantioselective catalysis. Tridentate diamine/phenol ligands have been successful. Give an example.
28. For the addition of organomagnesium compounds to arylmethylketones, the TADDOL ligand is advised (among others). TADDOL is also important in other enantioselective reactions. Structure?
29. Which product class would you expect on addition of arylmagnesiumbromides to arylnitrones? What is a nitrone? Would imines react even faster?
30. Do you know examples where reactions of organomagnesium reagents have to be catalyzed by transition metals?
31. Reaction of PhMgBr with chloroethene? Something is missing.
32. Reaction of (*S*)-(1-phenylbutan-2-yl)magnesium chloride with bromoethene in the presence PdCl₂(dppf)? Structures.
33. How would you cross-couple methyl *p*-chlorobenzoate with *n*-hexylMgBr?
34. Give an example of a carbomagnesiation of an alkyne.
35. Which partial structure is formed on Ti-catalyzed cross-cyclomagnesiation of allenes? Any carbons lost?
36. How did Frankland synthesize diethyl zinc? Geometry?
37. Why is the Reformatsky reaction possible with Zn, but not with Mg metal? Product?
38. Give the stoichiometries of two higher-order zincates. Are they more or less reactive than "regular" organozinc compounds?
39. Reaction of indene with (i) K in THF, (ii) ZnCl₂, and (iii) 3-picoline gave a mixture of enantiomers, but no *meso* compound.
40. Draw the preferred Zimmerman-Traxler transition state of the reaction of (*Z*)-crotylzincbromide and benzaldehyde. Product?

41. Use of dimethylaminoisoborneol as ligand in the reaction of PhCHO with Et₂Zn led to the phenomenon of "chiral enhancement". Explain. Structure.
42. What is the difference between the regular and the Furukawa version of the Simmons-Smith reaction? Starting material: 3-cyclopentenol.
43. Simmons-Smith reaction of (*R,E*)-pent-3-en-2-ol?
44. Give two examples of enantioselective Simmons-Smith reactions starting from cinnamyl alcohol.
45. 6-Iodo-1-hexene was reacted (i) with Et₂Zn, cat. PdCl₂(dppf), then (ii) with cyclohexenone. How many stereoisomers do you expect?
46. What does a Ziegler-Natta polymerization do? Ingredients? Importance?
47. Difference between Tebbe and Petasis reagents? Synthesis?
48. Which product do you expect on reaction of acetophenone and Cp₂Ti(C₃H₅)₂, NaHCO₃, PhMe?
49. It is searched for a two-step conversion of tetrahydro-2*H*-pyran-2-one to 4-oxaspiro[2.5]octane.
50. Kulinkovich reaction afforded 1-ethylcyclopropan-1-ol, starting from which compounds? Draw the widely accepted mechanism.
51. There are also enantioselective Kulinkovich reactions.
52. Conduct a McMurry coupling of hexandial. Zn/Cu pair: more Zn or more Cu?
53. What is Nugent's reagent and what is formed from it *in situ*?
54. And now the Schwartz reagent: Structure? React oct-4-yne with Cp₂ZrCl₂, DIBAL-H, and I₂!
55. What happens on reaction of EtZrCp₂Cl₂ with crotonic acid thiol ester in the presence of CuCl, AgOTf, and TMSCl in the presence BINOL-based phosphoramidite ligands, followed by LiAlH₄ reduction? What is a phosphoramidite?
56. How would you make SmI₂ *in situ*? Which effect will the addition of DMPU (structure?) have on the reduction potential?
57. Which products are formed from anthracene and stilbene with SmI₂ in water?
58. By which mechanism occurs pinacol coupling with SmI₂? What is a ketyl radical?
59. Treatment of 5-(2-ethynylphenyl)pentan-2-one with SmI₂ in *t*-BuOH/THF/HMPA has afforded a benzocyclooctene derivative. Please outline the mechanism to the very end.
60. SmI₂ can also be used in a catalytic manner, e. g., in the presence of excess Mg. What do you expect starting from ethyl 2-acetyl-2-methyl-5-oxopentanoate?
61. Outline the mechanism of the Hosomi-Sakurai reaction of allyltrimethylsilane and (*E*)-4-phenylbut-3-en-2-one.
62. Methyl pyruvate can serve as partner in a Cu-catalyzed, enantioselective variant of the Hosomi-Sakurai reaction. A chiral bisoxazoline ligand can be employed. Basic structure?

63. An earlier catalyst for the hydrosilylation of alkenes has been Karstedt's catalyst, which was largely replaced by Marko's catalyst. Which metal in which oxidation state do both catalysts contain? The structure of at least one would be good.
64. A key application of hydrosilylation in natural product synthesis is the conversion of alkyne to (*E*)-alkene moieties. How?