

1. This functional group was installed in the first step of an incorrect synthesis of glabrescol. The Corey, Noe, and Lin reaction regio- and enantioselectivity installs this functional group and uses an improved phthalazine containing ligand. E.J. Corey proposed the correct mechanism for a reaction installing this function group in which a metalate ester is produced directly via [3+2] cycloaddition. A reagent mixture containing a *bis*-cinchona alkaloid ligand and potassium ferricyanide as an oxidant can install this group asymmetrically. That mixture comes in alpha and beta forms and was developed by Sharpless. This functional group is installed in the reaction between osmium tetroxide and an alkene. For 10 points, name this functional group which contains two alcohols on neighboring carbons.  
ANSWER: **vicinal diol** (accept **1,2-diol**; accept **glycol**; prompt on “diol” or “syn-diol” by asking “what positional relation does the diol have?”; do not accept any other type of diol)

2. This scientist used tin triflate and titanium tetrachloride to generate *anti-syn* and *syn-syn* stereotetrads from  $\beta$  ketoimides. The first synthesis of vancomycin was reported by this scientist's group. That synthesis made use of this scientist's auxiliary to synthesize unnatural amino acids in high enantio- and diastereoselectivity. This scientist names two different reactions that convert  $\beta$ -hydroxy ketones to *anti*-diols: one uses tetramethyl ammonium triacetoxo borohydride and the other uses samarium iodide. Those two reactions are co-named for Saksena and Tishchenko. This scientist discovered that dibutyl boron triflate selectively formed (*Z*) enolates. For 10 points, name this Harvard chemist who developed oxazolidinone based auxiliaries for enantioselective aldol chemistry. ANSWER: David **Evans**

3. Iron contamination will hinder this reaction because it accelerates formation of a strong base from the reagents. Arthur Schultz developed an asymmetric version of this reaction using a proline derived amide auxiliary. A variant of this reaction was developed after it was observed that 1,4 dihydrobenzoic acid derivatives were selectively alkylated at the  $\alpha$ -carbon. The conditions used in this reaction notoriously turn PTFE stir bars black. The conditions used in this reaction can also be used to perform conjugate reduction on  $\alpha$ - $\beta$  unsaturated ketones and to reduce alkynes to the trans alkene. Solvated electrons form a deep-blue color in a solution that performs this reaction. For 10 points, name this reaction that reduces arenes to 1,4 cyclohexadienes with an alkali metal in liquid ammonia.  
ANSWER: **Birch** reduction (accept **Birch** alkylation; prompt on “dissolving metal reduction”)

4. In his group's synthesis of onocerin, E. J. Corey developed a method to convert silyl enol ethers to this functional group without the use of alkyl lithium reagents. Though the oxazolidinone derived enolates are normally unreactive towards secondary or  $\beta$ -branched electrophiles, this functional group can be added to the electrophiles to overcome that underactivity. A methyl derivative of this functional group, which is similar in structure to magic methyl, *O* alkylates enolates. An electrophilic source of this functional group is Comins' reagent. This sulfonate derivative is more reactive than the corresponding bromide but less than the iodide in cross-coupling reactions. For 10 points, name this functional group derived from trifluoromethanesulfonic acid.  
ANSWER: **triflate** (accept **trifluoromethanesulfonate** until mentioned)

5. The less substituted version of this functional group is synthesized by photorearrangement of spiro-oxaziridines. NMP, a safer alternative to HMPA, contains this functional group. This functional group can be synthesized by reacting an imine with a ketene. Woodward and Robinson feuded over the structure of a molecule now known to contain this functional group. John Sheehan's synthesis of that molecule featured one of the first uses carbodiimide coupling. This functional group can be produced by Beckmann rearrangement of an oxime derived from a cyclic ketone. Nylon 6 is synthesized from a 7-membered version of this functional group through ring-open polymerization. For 10 points, name this functional group whose four membered variety names a class of antibiotics.  
ANSWER: **lactam** (accept **cyclic amide**; prompt on “amide”)

6. Higher order reagents containing this element perform suprafacial  $S_N2'$  displacements. Those reagents, which

were developed by Bruce Lipshutz, contain a nontransferrable 2-thienyl ligand. Lipshutz also developed a “hot” version of a reagent containing this element’s hydride, Stryker’s reagent. BOX ligands are most commonly used with this metal. Aryl radicals are generated *in situ* and substituted in a reaction catalyzed by this metal. This metal catalyzes acetylenic coupling reactions like the Cadiot–Chodkiewicz and Glaser couplings. Diazonium salts are halogenated in the Sandmeyer reaction, which uses halide salts of this metal. Salts of this metal can be added to a reaction mixture to favor conjugate addition. For 10 points, name this metal that is found with lithium in Gilman reagents.

ANSWER: **copper** (prompt on “lithium” by asking “what is the other metal in those reagents”)

7. A reaction of this type is performed by reacting an amine with a peracid then heating the reaction mixture. One reaction in this class involves a xanthate ester formed by reaction of an alkoxide, carbon disulfide, and methyl iodide. Unlike Martin’s Sulfurane, Burgess’ reagent affects a reaction of this type. It’s not a reduction, but  $\beta$  substituted enones reverse stereochemistry during Heck coupling because the final step is this type of reaction. Aerobic oxidation of selenides is followed by a reaction of this type that commonly used to prepare  $\alpha$ - $\beta$  unsaturated carbonyls. The Cope, Chugaev, and Selenoxide reaction are all this type of elimination. For 10 points, name this class of reactions in which two vicinal groups leave from the same side of the bond and leave behind an alkene.

ANSWER: **syn-elimination** (accept thermal or pericyclic **syn-elimination**; accept **E<sub>i</sub>** reaction; prompt on “elimination;” prompt on “ $\beta$ -elimination”)

8. The key reagent for this reaction can be synthesized by subjecting Bestmann’s reagent to the Roskamp reaction. Though this reaction is normally run with sodium hydride, addition of lithium chloride allows one to run this reaction with an amine base in the Masamune-Roush modification. This reaction can be performed enantioselectively with ketones with chiral phosphoramidates. A trifluoroethanol derivative of the key reagent reverses the stereoselectivity of this reaction in the Still-Genari modification. Reacting a trialkyl phosphite with an  $\alpha$ -halo ester synthesizes a key reagent for this reaction. That synthesis is the Michaelis-Arbusov reaction. For 10 points, name this variant of the Wittig olefination that uses a ylide derived from a stabilized phosphonate ester.

ANSWER: **Horner-Wadsworth-Emmons** olefination (accept **HWE** olefination; accept **Still-Genari** before mentioned; prompt on “Wittig olefination” or “Wittig reaction” with “what modification of the Wittig olefination”)

9. A group with 4 atoms of this element is notably stable towards the Jones reagent and is instead removed by brief exposure to UV light. It’s not boron, but tributyltin oxide can be converted to tributyltin hydride with a reagent containing this element. It’s not tin, but reagents containing this element can be used as hydride sources in radical reductions. 2,6-lutidine is used with triflate derivatives of reagents containing this element. The chloride derivative of those reagents is used with imidazole, a protocol developed by E. J. Corey. A reagent containing this element allylates carbonyls in the Sakurai reaction. Protecting groups containing this element are commonly removed with a fluoride source such as TBAF. For 10 points, name this element found in the TBS protecting group. ANSWER:

**silicon**

10. A reagent with this functionality selectively deprotects TES ethers over TBS ethers. Nicolaou and Baran used a reagent with this functionality to synthesize  $\alpha$ - $\beta$  unsaturated carbonyls and aryl aldehydes, though those reactions are notoriously difficult to reproduce. EBX reagents, which contain this functionality, are used in electrophilic alkynylation. The second step of the Lemieux–Johnson oxidation uses a reagent with this functionality. A reagent with this functionality is synthesized from a benzoic acid derivative and oxone. Acetylating that reagent creates Dess-Martin’s reagent. It’s not lead tetraacetate or permanganate, but a compound containing this functionality cleave glycols. For 10 points, name these compounds that contain iodine in an abnormally high oxidation state.

ANSWER: **hypervalent iodine** (accept **DMP** before “Dess-Martin;” accept **iodane**; accept **periodinane**; accept **IBX**; accept **periodate**; accept **periodic acid**)

11. It's not BINAP, but this compound has been added to Raney nickel to enantioselectively reduce  $\beta$ -keto esters. Acetonides of this compound can be converted to the TADDOL and DIOP ligands. André Charette has used dioxaborolanes formed from amide derivatives of this compound as a chiral auxiliary. Acetals formed from this compound and  $\alpha$ - $\beta$  unsaturated carbonyls undergo asymmetric cyclopropanation. It's not  $\alpha$ -pinene, but boron derivatives of this compound perform enantioselective allylations and crotylations in the Roush reaction. The diethyl or diisopropyl ester of this compound, *tert*-butanol, and titanium isopropoxide catalyze the Sharpless epoxidation. For 10 points, name this compound whose crystals were famously sorted by Pasteur in the first chiral resolution. ANSWER: **tartaric acid** (accept **tartrate**)

12. Walter Trahanovsky used a reagent containing this element to synthesize benzaldehydes from methyl arenes. A reagent synthesized by dissolving this element's oxide in nitric acid is preferred over manganese triacetate for generating radicals. Zhiwei Zuo used catalysts containing this lanthanide to functionalize methane and other gaseous alkanes through photoredox catalysis. Hydrocarbon derivatives of this element are nonbasic nucleophiles. This element can stably exist in both the +3 and +4 oxidation states, which makes it useful in single electron reactions. A compound containing this element is the most common Lewis acid used to synthesize allylic alcohols from enones. For 10 points, name this element whose trichloride derivatives is used in the Luche reduction. ANSWER: **cerium**

13. Lewis Sarrett led a team at this company that completed the first total synthesis of cortisone. This company produced the first doses of penicillin used to treat US patients at MassGeneral Hospital following the Cocoanut Grove fire in Boston. This company published the first crystal structure of HIV protease and developed indinavir at its Rahway and West Point locations respectively. While scaling up production of its second most profitable drug as of 2019, this company developed two different methods for enantioselective reduction of a  $\beta$ -keto amide. The first is a rhodium catalyzed enamine hydrogenation, and the second is a PLP mediated transamination *en route* to Januvia. For 10 points, name this company that has feuded with a German company over legal rights to their shared name. ANSWER: **Merck & Co.** (or **Merck Sharp & Dohme** or **MSD**)

14. As of 2016, this scientist's namesake reaction is the second most used cross coupling reaction in pharmaceutical syntheses falling between the Suzuki and Sonogashira reactions. This scientist developed precatalysts that are air, moisture, and thermally stable. Those precatalysts are complexed with monodentate phosphine ligands and reductively eliminate carbazole to form active Pd(0) species. This scientist developed a class of ligands whose members are named after students like David Old and John Wolfe and cats like Trixie and Rufus. Those bulky dialkylbiaryl phosphine ligands prevent Pd black precipitation in cross-coupling reactions. For 10 points, name this organometallic chemist who developed the field of arene-heteroatom couplings in parallel with John Hartwig. ANSWER: Stephen L. **Buchwald**

15. Kuniaki Tatsuta synthesized the namesake compound of this class of molecules starting from D-glucosamine, which formed the A-ring. A company founded by Andrew Myers synthesizes compounds in this family using a Michael-Dieckmann annulation to bring together diverse D-ring precursors and AB-enones. The final step in that synthetic platform was developed by Gilbert Stork and is a hydrogenation of a 3-benzyloxyisoxazole to reveal the  $\beta$  keto amide of the A-ring. Pfizer determined the structure of terramycin through a collaboration with R. B. Woodward who went on to complete the first total synthesis of a compound in this class, a 6-demethyl-6-deoxy derivative. For 10 points, name this class of antibiotics that includes aureomycin and doxycycline. ANSWER: **tetracyclines** (prompt on "antibiotics;" prompt on "eravacycline")