

Orgo

Harrison Wang

1. According to Grossman, tert-butanol is less acidic than ethanol due to solvent effects and not this phenomenon, because in the gas phase t-BuOH is actually more acidic. Fundamentally, downshifts in proton NMR result from this non-resonance effect. This effect causes the otherwise-unusual hydrogen bonding of the hydrogen in chloroform, which in turn causes a chloroform-acetone azeotrope. TFA has a pKa around 0 because of this effect, where the pKa of (\*) acetic acid is reduced by around one every time another fluorine atom is added to the alpha carbon. This effect is a result of non-resonance-structure EWGs, which often have very high electronegativities. For ten points, give this effect, a result of pulling sigma bond electron density toward electronegative atoms.

ANSWER: inductive effects, stabilization, etc

[10] Reacting to completion a methyl ketone with bromine and strong base allows this yellow liquid to form, whose deprotonated form is much, much easier to be displaced than deprotonated methane due to inductive effects.

ANSWER: bromoform (or tribromomethane or CHBr<sub>3</sub> or equivalents)

2. One cyclic species of this type is produced before water is eliminated in the Feist-Benary synthesis. Another cyclic functionality of this type is found in 3,4-DHP, used to protect alcohols. One of these species and a ketone are found in a chair conformation transition state that is used to predict the reaction's stereochemical outcome. Nucleophilic attack by this species on a silyl chloride forms a certain (\*) ether of this name. Because of the need to establish aromaticity, 2,4-cyclohexadienone rapidly converts to one of these species. The first step of the acid-catalyzed production of these species protonates the oxygen, then deprotonates the alpha carbon, forming a C-C double bond. For ten points, name this functionality produced from tautomerization of a ketone.

ANSWER: enolate (accept enol ether; prompt on alkene or alcohol, I guess)

[10] Silyl enol ethers are used as the nucleophile in a modified aldol condensation named after this Japanese guy.

ANSWER: Teruaki Mukaiyama

3. Because of Zr(IV)'s extreme propensity to undergo one type of these reaction steps, and then a reinsertion, hydrozirconations of internal alkenes leads to terminal alkylzirconium compounds. One might add triethylamine, which reacts with an otherwise-unreactive Pd(II), to form the active Pd species and an iminium ion byproduct in this type of reaction step. The two reactants that are to be coupled in a palladium-catalyzed cross-coupling reaction are (\*) removed from the coordination complex in this type of reaction step, forming the product. In those reactions, this step comes after oxidative addition and transmetalation. For ten points, name this reaction step that usually comes at the end of a catalytic cycle, which comes in "beta-hydride" and "reductive" types.

ANSWER: elimination (accept more specific answers; prompt on reduction)

[10] In this type of elimination, a hydrogen on a carbon in a carbon-metal single bond is kicked off by electrons from the metal, then, the hydrogen bonds to the metal atom, which, interestingly, is an oxidation. This type of elimination occurs in the Green mechanism of tantalum-catalyzed Ziegler-Natta polymerization.

ANSWER: alpha-hydride elimination

4. This scientist is the first namesake of a catalyst that works by coordinating its nitrogen to borane, and coordinating its boron to a ketone, then effecting a hydride transfer, leading to chiral reduction of the ketone to an alcohol. This man pioneered the use of TBAF to desilylate alcohols. This guy is the alphabetically-prior namesake of a reaction that reacts an aldehyde with a phosphonium ylide derived from carbon tetrahalide to form a dibromoalkene, which is then reduced to an (\*) alkyne. This man used the CBS reduction in his classical prostaglandin syntheses. For ten points, name this pioneer of retrosynthetic organic chemistry and 1990 Nobel Prize winner.

ANSWER: EJ Corey

[10] The CBS reduction, though sometimes named for Shinichi Itsuno, is also named for EJ Corey and these other two people.

ANSWER: Raman K Bakshi and Saizo Shibata

5. In one reaction of this class, a namesake ester is radically cleaved, but preceding that step is a coupling of an aromatic thioamide. 2-pyrone derivatives commonly are cycloadded with dienophile alkynes, and then form an aromatic compound by immediately undergoing this type of reaction. To ultimately acetylate a compound in the acetoacetic ester synthesis, this /last/ step must be performed. This (\*) extrusion of a certain gas often

requires a carbonyl alpha to the gas-producing functionality and can be induced by heat along with strong acid or strong base. To arrive at an amine in one variant of the Schmidt reaction, the carboxylic acid group is removed using this type of reaction. For ten points, name this class of reactions that evolve CO<sub>2</sub> from a molecule.

ANSWER: decarboxylation (prompt on stuff like **elimination**, extrusion of a **gas**, **carbon dioxide** or **CO<sub>2</sub>** before mention)

[10] Radical intermediates, such as the tributyltin radical, attack an atom of this element in the first propagation step of the Barton-McCombie decarboxylation. Xanthates possess a carbon single bonded to one atom of this element and double bonded to another of this element.

ANSWER: Sulfur

6. **The germanium atom is bonded to a group with this property in a 2001-synthesized germanaphthalene derivative, leading to its stability. Carbynes, long chains of alternating single and triple bonded carbons, are pretty stable if they are terminated by groups with this property. A modification of the Wittig reaction uses an alkoxide base with this property to specifically synthesize E alkenes. Bases with this property, such as LiHDMS, are used for alpha carbon chemistry because their (\*) non-nucleophilicity is a result of this property. Tetra-tert-butyl methane is not synthesizable because of the size of the tert-butyl groups, resulting in this property. For ten points, name this property of large functional groups hindering the action of other groups.**

ANSWER: high steric effects, hindrance, etc. (accept bulky, prompt on **high strain** or **unreactive** or stuff)

[10]The reagent di-tert-butyl carbonate is used to protect amines by forming this protecting group, which contains a carbamate functionality.

ANSWER: tert-butyloxycarbonyl

7. **Three equivalents of one of these reagents reduce an ortho-substituted nitroarene to an indole in a reaction named for Bartoli. Instead of the intended reaction, a concerted beta-hydride reduction may occur between a sterically-hindered electrophile and one of these reagents. A Weinreb amide, instead of an ester or acid chloride, is implemented to prevent multiple substitutions by one of these (\*) halogen-containing reagents. Reacting a nitrile with one of these reagents, followed by workup, forms a ketone. To synthesize carboxylic acids, just put some turnings of a certain metal into a solution of alkyl halide to form some of these reagents, then dump the solution onto some dry ice. For ten points, name this class of alkylmagnesium halide reagents.**

ANSWER: Grignard reagents

[10] Grignard reagents usually add to the carbonyl carbon of an alpha-beta unsaturated ketone, but if transmetalated with this most commonly-used metal, it will add to the beta carbon.

ANSWER: copper (b/c Gilman)

8. **In December 2016, Cerutti-DeLaSalle et al used this technique directly coupled to olfactometry to discover some long aliphatic cyclopropanecarboxylic acid species. One part used in this technique may come in WCOT or SCOT types, depending on if they contain a solid support, and that part may also be “packed” with diatomaceous earth for maximization of surface area. One detector used in this technique measures changes in heat flow and is called a (\*) TCD. For injecting analytes in this technique, a microliter syringe is used, otherwise the thin, coiled columns utilized in this technique may overload. The analyte adsorbs to the stationary phase, while the mobile phase in this technique is usually nitrogen, argon, or helium. Also coupled to mass spectrometry, for ten points, name this type of chromatography used for separation of vapor-phase mixtures.**

ANSWER: gas chromatography (accept gas-solid chromatography or gas-liquid chromatography because clues aren't the most unique; prompt on partial answer or **column chromatography** but not high profile liquid chromatography)

[10] In contrast to the thermal conductivity detector or the flame ionization detector, this type of detector uses a radioactive electron source to reduce electronegative organic species, like halogens and quinones, and measures the change in current.

ANSWER: electron capture detector

9. **This metal's chloride is used to catalyze a pinacol coupling in the ring B-closing step of Nicolaou's taxol synthesis. This metal is used in a catalyst that lines up a hydroperoxide with an allyl alcohol's carbon-carbon double bond, leading to a transfer of an oxygen to the alkene. One reaction utilizing this element reductively couples two ketones to form an alkene, and another, utilizing diethyl (\*) tartrate as chiral ligands, is an**

asymmetric epoxidation named for Sharpless. This non-aluminium metal is bound to two cyclopentadienyl ligands in two different carbonyl methylation reagents, the Petasis and Tebbe reagents. For ten points, name this metal with symbol Ti.

ANSWER: titanium (accept Ti before mention)

[10] In the Tebbe reagent, the active species is formed after dissociation of dimethylaluminum chloride and is this type of carbene. Other types of these carbenes may possess tantalum (V) centers.

ANSWER: Schrock carbene

*NOTE TO MODERATOR: the powermark in this question is in the middle of a word.*

10. A Grignard reagent reacted with an ester in the presence of titanium isopropoxide forms a derivative of this molecule. At high temperatures, vinyl derivatives of this molecule name a rearrangement that is posited to occur via a biradical mechanism. After reaction of butyllithium with dihalo derivatives of this molecule, allenes are made following elimination of lithium halide and rearrangement. (Iodomethyl)(\*)zinc iodide is an intermediate in a reaction that forms derivatives of this molecule from alkenes. Generally, reacting nucleophilic methyl derivatives with alkenes creates derivatives of these cyclic molecules. For ten points, name this simplest cycloalkane with very strained, 60 degree bond angles and formula C<sub>3</sub>H<sub>6</sub>.

ANSWER: cyclopropane

[10] This catalyst, comprised of manganese complexed to a salen-type ligand, is co-oxidized with bleach to asymmetrically epoxidate alkenes.

ANSWER: Jacobsen-Katsuki catalyst

11. Dropping a melting-point capillary down one of these apparati resting on the lab bench is one way to get a solid stuck at the top of the capillary to the bottom. In a simple standard inert atmosphere setup, the top of this apparatus is covered with a septum with a syringe poking through it. The functionality of one type of these devices results from “finger” protrusions in the glass. To completely fill a compartment in one type of these devices, (\*) water must flow into the bottom inlet and flow out the top inlet. In orgo labs, you may just not use this piece of equipment if you don’t have specialized short-path distillation apparati, and just use a distillation head and receiver without using the Liebig type of this glassware. For ten points, name these tubes used in reflux or distillation to cool vapors.

ANSWER: condenser

[10] This type of apparatus is basically a rod in which one can run through with coolant, and then stick inside the atmosphere of a reaction flask. The coiled type of these devices are named for Otto Dimroth and are usually used for refluxing.

ANSWER: cold finger

12. Use of this reagent, which demethylates PDMS surfaces, followed by KOH etch, leads to permanent hydrophilization of PDMS. Use of this reagent in silanol synthesis bypasses silyl chloride, instead acting on pure silicon or silicon dioxide. One variant of this reagent is used in the first step of the RCA procedure, is created by replacing one component of this mixture with ammonia, and is its (\*) “base” variant. This mixture will blow up if mixed with organic solvent, especially in some newsworthy accidents with acetone, since its power comes from its generation of atomic oxygen, which turns all the carbons into carbon dioxide. For ten points, give this mixture of sulfuric acid and hydrogen peroxide used for cleaning glassware and digesting hot dogs.

ANSWER: piranha solution, reagent, etch, etc.

[10] Datsyuk et al. showed that base piranha left the structure of these molecules intact, unlike “normal” piranha solution, which caused certain defects in the periodic structure of these materials. Base piranha also removed some impurities from these molecules, which can be confirmed by analysis of G and D bands in Raman spectroscopy.

ANSWER: carbon nanotubes, prompt on fullerenes

13. This compound is a byproduct of the most atom economic form of the rather benign aluminum-catalyzed MSPV reduction. Complete condensation of three molecules of this compound forms 1,3,5-trimethylbenzene. This compound’s peroxide is made from oxidative dimerization or trimerization and is used as an explosive. Reactions such as DIBAL-H reduction and metal-halogen insertion are commonly done along with cooling from a (\*) cold bath of this solvent, even though isopropanol apparently has an even lower freezing point. Wacker oxidation transforms propylene into this compound, but it’s more commonly industrially synthesized along with

phenol in the cumene process. Jones oxidation of isopropanol yields this compound. For ten points, name this solvent, with two methyl groups attached to a carbonyl carbon.

ANSWER: acetone (or 2-propanone)

[10] Somewhat surprisingly, someone names this reverse reaction of the equilibrium in the MSPV reduction.

ANSWER: Oppenauer oxidation

14. EJ Corey developed an important advance in the synthesis of these molecules by using pyridinethiols as substituents to effect ester formation. The last steps in Woodward's synthesis of an important class of these molecules were coupling two six-membered carbohydrate derivatives to the rest of the molecule. To create an all-E conjugated triene motif in one member of this class of molecules, Nicolaou ended his artful synthesis of that molecule with a famous (\*) Stille coupling. For ten points, name this class of compounds, which includes members such as rapamycin and erythromycin, often used as antibiotics.

ANSWER: macrolides; prompt on antibiotics

[10] In the Stille coupling in Nicolaou's total synthesis of rapamycin, an ethylene derivative functionalized with two of these groups is coupled to two vinyl iodides.

ANSWER: tributyltin (or tributylstannane or Bu<sub>3</sub>Sn or SnBu<sub>3</sub>, prompt on partial)

15. The "ultimate synthetic product" maitotoxin only has 12 atoms with this hybridization, even though it's, like, 3600 daltons heavy. Every carbon in a blue and unusually polar hydrocarbon has this hybridization. Atoms with this hybridization possess orbitals that classify electrocyclic reactions as conrotatory or disrotatory. A pretty notable rule states that (\*) bridgehead carbons cannot adopt this hybridization. Even though there is a lone pair attached to the nitrogen in amides and in aniline, resonance causes those nitrogens to have mostly this hybridization. For ten points, name this hybridization that has 33 percent s character and causes molecules to adopt a trigonal planar geometry.

ANSWER: sp<sup>2</sup> hybridization

[10] Azulene, an isomer of naphthalene, is polar because it has a resonance form in which electrons are redistributed to establish this characteristic.

ANSWER: aromaticity

16. In the 1979 /Angewandte Chemie/ paper introducing this idea, six principal methods of accomplishing this are listed, including electro- and photochemical redox. In retrosynthetic analysis, splitting a molecule across 1,2 or 1,4 functionalities into two synthons that differ only by charge, requires the application of this concept in the forward synthesis. One synthesis technique utilizing this concept starts with protection of a carbonyl with a (\*) dithiane. In a famous demonstration of this concept, cyanide can attack an electrophilic carbonyl carbon, resulting in an intermediate with that attacked carbon now becoming nucleophilic, in the benzoin condensation. For ten points, give this German word meaning reversal of polarity.

ANSWER: umpolung

[10] This guy wrote the pioneering /Angewandte Chemie/ paper after developing umpolung with EJ Corey. He also names a polymolybdic acid-based "Magic" stain.

ANSWER: Dieter Seebach

*NOTE TO MODERATOR: Read first sentence slowly, with pauses at each plus sign.*

17. Pencil and paper ready. In an alpha-beta unsaturated ketone, this functional group is added to the alpha carbon (+) by first trapping the enol, (+) then epoxidating the C-C double bond, (+) then reforming the ketone. (+) Selenium dioxide can be used to install one of these functionalities one carbon away from a carbon-carbon double bond. These groups may be converted to bromides using phosphorus tribromide, to chlorides using (\*) thionyl chloride, or to tosylates using tosyl chloride, since they are terrible leaving groups in S<sub>N</sub>2 reactions. Ether cleavage using hydrohalic acids form an alkyl halide and one of these species. These species may be coupled to carboxylic acids to form esters. For ten points, name this functional group abbreviated OH.

ANSWER: alcohol (accept hydroxyl group or something, prompt on alkoxide)

[10] The methyl substituent in a tosylate group is replaced with a bromide substituent in this variant, making this leaving group even better.

ANSWER: brosylate