Cyclopropane ring formation

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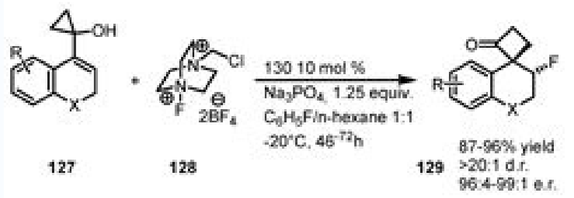
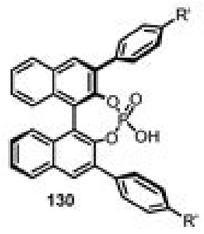
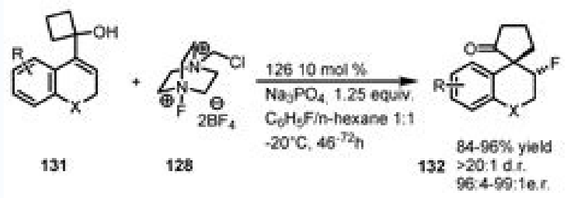
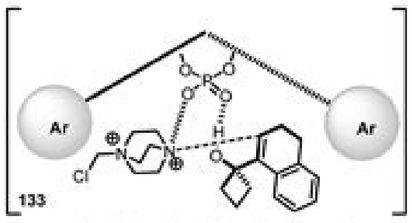
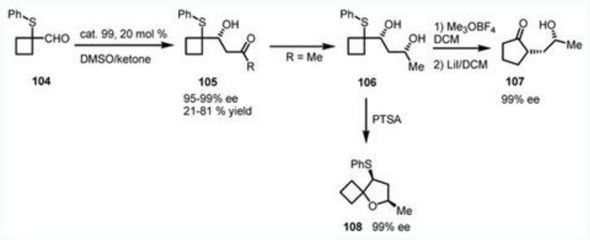


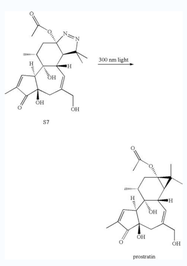




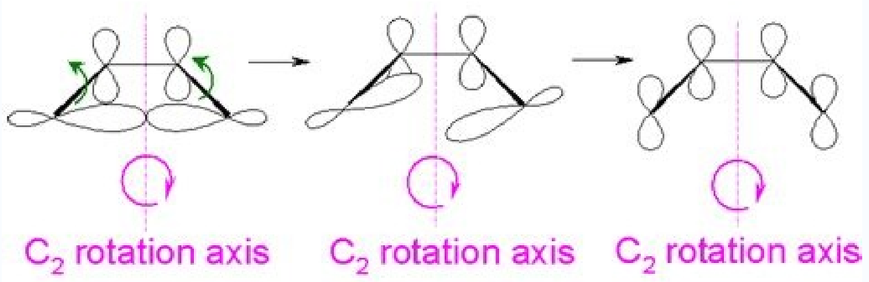


mechanistic rationale for the observed *Re*-facefluorination with R_a-configured phosphate anion

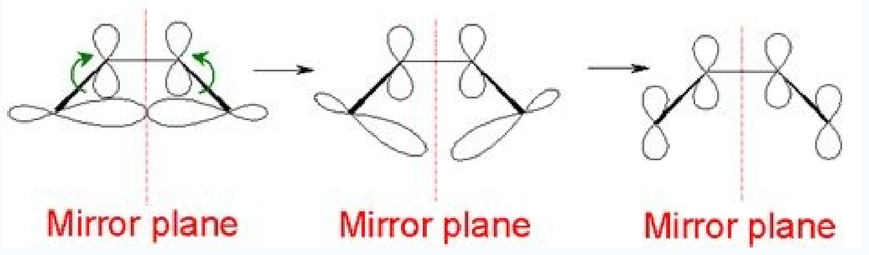


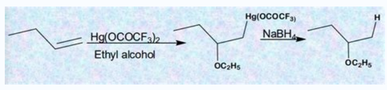


Conrotatory ring opening: a twofold (C_2) rotation axis is present throughout the reaction



Disrotatory ring opening: a mirror plane (for reflection) is present throughout the reaction





What is the angle strain in cyclopropane. Cycloalkanes in order of increasing ring strain. Cyclopropane ring formation in membrane lipids of bacteria. Ring opening reactions of cyclopropane.

It has been known for several decades that cyclopropane fatty acids (CFAs) occur in the phospholipids of many species of bacteria. CFAs are formed by the addition of a methylene group, derived from the methyl group of S-adenosylmethionine, across the carbon-carbon double bond of unsaturated fatty acids (UFAs). The C1 transfer does not involve free fatty acids or intermediates of phospholipid biosynthesis but, rather, mature phospholipid molecules already incorporated into membrane bilayers. Furthermore, CFAs are typically produced at the onset of the stationary phase in bacterial cultures. CFA formation can thus be considered a conditional, postsynthetic modification of bacterial membrane lipid bilayers. This modification is noteworthy in several respects. It is catalyzed by a soluble enzyme, although one of the substrates, the UFA double bond, is normally sequestered deep within the hydrophobic interior of the phospholipid bilayer. The enzyme, CFA synthase, discriminates between phospholipid vesicles containing only saturated fatty acids and those containing UFAs; it exhibits no affinity for vesicles of the former composition. These and other properties imply that topologically novel protein-lipid interactions occur in the biosynthesis of CFAs. The timing and extent of the UFA-to-CFA conversion in batch cultures and the widespread distribution of CFA synthesis among bacteria would seem to suggest an important physiological role for this phenomenon, yet its rationale remains unclear despite experimental tests of a variety of hypotheses. Manipulation of the CFA synthase of Escherichia coli by genetic methods has nevertheless provided valuable insight into the physiology of CFA formation. It has identified the CFA synthase gene as one of several rpoS-regulated genes of E. coli and has provided for the construction of strains in which proposed cellular functions of CFAs can be properly evaluated. Cloning and manipulation of the CFA synthase structural gene have also enabled this novel but extremely unstable enzyme to be purified and analyzed in molecular terms and have led to the identification of mechanistically related enzymes in clinically important bacterial pathogens. The highly strained nature of cyclopropane compounds makes them very reactive and interesting synthetic targets. Additionally cyclopropanes are present in numerous biological compounds. One common method of cyclopropane synthesis is the reaction of carbenes with the double bond in alkenes or cycloalkenes. Methylene, H2C, is simplest carbene, and in general carbenes have the formula R2C. Other species that will also react with alkenes to form cyclopropanes but do not follow the formula of carbenes are referred to as carbenoids. Carbenes were once only thought of as short lived intermediates. The reactions of this section only deal with these short lived carbenes which are mostly prepared in situ, in conjunction with the main reaction. However, there do exist so called persistent carbenes. These persistent carbenes are stabilized by a variety of methods often including aromatic rings or transition metals. In general a carbene is neutral and has 6 valence electrons, 2 of which are non bonding. These electrons can either occupy the same sp2 hybridized orbital to form a singlet carbene (with paired electrons), or two different sp2 orbitals to from a triplet carbene (with unpaired electrons). The chemistry of triplet and singlet carbenes is quite different but can be oversimplified to the statement: singlet carbenes usually retain stereochemistry while triplet carbenes do not. The carbenes discussed in this section are singlet and thus retain stereochemistry. The reactivity of a singlet carbene is concerted and similar to that of electrophilic or nucleophilic addition (although, triplet carbenes react like biradicals, explaining why sterochemistry is not retained). The highly reactive nature of carbenes leads to very fast reactions in which the rate determining step is generally carbene formation. The preparation of methylene starts with the yellow gas diazomethane, CH2N2. Diazomethane can be exposed to light, heat or copper to facilitate the loss of nitrogen gas and the formation of the simplest carbene methylene. The process is driven by the formation of the nitrogen gas which is a very stable molecule. A carbene such as methlyene will react with an alkene which will break the double bond and result with a cyclopropane. The reaction will usually leave stereochemistry of the double bond unchanged. As stated before, carbenes are generally formed along with the main reaction; hence the starting material is diazomethane not methylene. In the above case cis-2-butene is converted to cis-1,2-dimethylcyclopropane. Likewise, below the trans configuration is maintained. In addition to the general carbene with formula R2C there exist a number of other compounds that behave in much the same way as carbenes in the synthesis of cyclopropane. Halogenated carbenes are formed from halomethanes. An example is dicholorcarbene, Cl2C. These halogenated carbenes will form cyclopropanes in the same manner as methylene but with the interesting presence of two halogen atoms in place of the hydrogen atoms. Carbenoids are substances that form cyclopropanes like carbenes but are not technically carbenes. One common example is the stereospecific Simmon-Smith reaction which utilizes the carbenoid ICH2ZnI. The carbenoid is formed in situ via the mixing of a Zn-Cu couple with CH2I2.Since this reacts thesame as a carbene, the same methods can be applied to determine the product. An example of this is given as problem 5. 1. Knowing that cycloalkenes react much the same as regular alkenes what would be the expected structure of the product of cyclohexene and diazomethane facilitated by copper metal? 2. What would be the result of a Simmons-Smith reaction that used trans-3-pentene as a reagent? 3. What starting material could be used to form cis-1,2-diethylcyclopropane? 4. What would the following reaction yield? 5. Draw the product of this reaction. What type of reaction is this? 1. The product will be a bicyclic ring, Bicyclo[4.1.0]heptane. 2. The stereochemistry will be retained making a cyclopropane with trans methyl and ethyl groups. Trans-1-ethyl-2-methylcyclopropane 3. The cis configuration will be maintained from reagent to product so we would want to start with cis-3-hexene. A Simmons Smith reagent, or methylene could be used as the carbene or carbenoid. 4. The halogenated carbene will react the same as methylene yielding, cis-1,1-dichloro-2,3dimethylcyclopropane. 5. This is a Simmons-Smith reaction which uses the carbenoid formed by the CH2I2 and Zu-Cu. The reaction results in the same product as if methylene was used and retains stereospecificity. Iodine metal and the Zn-Cu are not part of the product. The product is trans-1,2-ethyl-methylcyclopropane. References Vollhardt, K. Peter C. and Schore, Neil E. Organic Chemistry: Structure and Function. New York: Bleyer, Brennan, 2007. Abdel-Wahab, Aboel-Magd A. Ahmed, Saleh A. and Dürr, Heinz. "Carbene Formation by Extrusion of Nitrogen" in CRC Handbook of Organic Photochemistry and Photobiology. CRC Press, 2004. Contributors A large chunk of Earth's earthquakes and volcanic eruptions occur in a narrow zone around the Pacific Ocean known as the "Ring of Fire." Scientists are only just beginning to understand why this tectonic explosivity is so confined.A new study has uncovered part of the answer for why the Ring of Fire, and other volcanic arcs around the world, occur in the narrow spaces that they do.It has to do with the complicated and varying recipe of liquid, hot magma and cooling water that combine beneath the Earth's crust to cause a volcanic eruption.Researchers have known for decades that curving chains of volcanoes, or volcanic arcs — such as the Aleutian Islands off the coast of Alaska — form where tectonic plates interact."It has been recognized for almost 50 years that the volcanic arcs form where one oceanic plate sinks beneath another," said Phillip England of Oxford University in England."But while many models of this process have been put forward, none has been able to explain the location, and narrowness, of the volcanic arcs," England said.Scientists do know why eruptions of peaks along these volcanic arcs are extremely violent. The molten rock contains a high proportion of water which, as superheated gas, provides the power for the explosive eruptions. In addition, the presence of the water lowers the melting temperature of the rock, which aids the transformation from solid rock to hot, liquid magma — a necessary ingredient for volcanoes."Most previous explanations for the origins of volcanoes suggested that this kind of 'wet' melting is responsible for getting a volcano started," said Richard Katz, also of Oxford.However, it turns out that water mixes in with the molten rock in fairly broad regions of the Earth's mantle, so the mere presence of water doesn't explain why the volcanic chains are so narrow."We noticed that there is a very simple geometrical pattern in the distribution of the volcanoes which provides a powerful clue as to what is going on," Katz said.Using a mathematical model of heat transport in the regions where two plates collide, the Oxford team showed that the observed geometrical pattern can only be explained if the volcanoes are localized above the few narrow regions in which mantle melts, seemingly paradoxically, in the absence of water.These limited spots of water-free rock melt then blaze a trail through the Earth's mantle up to the surface, and explosive water-laden magma follows, allowing for the violent eruptions.In addition to hosting devastating eruptions, the volcanic chains hold valuable clues to the evolution of the earth, because they are the surface expressions of a gigantic chemical factory in which molten rock separates from the mantle to solidify as the crust we live on, and from which significant volumes of gas are emitted into the atmosphere.Katz, England and their colleagues now intend to investigate the implications of their results for the chemical processes happening deep beneath the volcanic chains.The findings are published in the Oct. 7 issue of the journal Nature.This article was provided by OurAmazingPlanet, a sister site to LiveScience.

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