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Stereospecific reaction example

Illustrated Glossary of Organic Chemistry In chemistry, stereospecificity is the property of a reaction mechanism that leads to different stereoisomeric reaction products from different stereoisomeric reactants, or which operates on only one (or a subset) of the stereoisomers.[1][2][3] In contrast, stereoselectivity[1][2] is the property of a reactant mixture where a non-stereospecific mechanism allows for the formation of multiple products, but where one (or a subset) of the products is favored by factors, such as steric access, that are independent of the mechanism. A stereospecific mechanism specifies the stereochemical outcome of a given reactant, whereas a stereoselective reaction selects products from those made available by the same, non-specific mechanism acting on a given reactant. Given a single, stereoisomerically pure starting material, a stereospecific mechanism will give 100% of a particular stereoisomer (or no reaction), although loss of stereochemical integrity can easily occur through competing mechanisms with different stereochemical outcomes. A stereoselective process will normally give multiple products even if only one mechanism is operating on an isomerically pure starting material. The term stereospecific reaction is ambiguous, since the term reaction itself can mean a single-mechanism transformation (such as the Diels-Alder reaction), which could be stereospecific, or the outcome of a reactant mixture that may proceed through multiple competing mechanisms, specific and non-specific. In the latter sense, the term stereospecific reaction is commonly misused to mean highly stereoselective reaction. Chiral synthesis is built on a combination of stereospecific transformations (for the interconversion of existing stereocenters) and stereoselective ones (for the creation of new stereocenters), where also the optical activity of a chemical compound is preserved. The quality of stereospecificity is focused on the reactants and their stereochemistry; it is concerned with the products too, but only as they provide evidence of a difference in behavior between reactants. Of stereoisomeric reactants, each behaves in its own specific way. Stereospecificity towards enantiomers is called enantiospecificity. Examples Nucleophilic substitution at sp³ centres can proceed by the stereospecific S_N2 mechanism, causing only inversion, or by the non-specific S_N1 mechanism, the outcome of which can show a modest selectivity for inversion, depending on the reactants and the reaction conditions to which the mechanism does not refer. The choice of mechanism adopted by a particular reactant combination depends on other factors (steric access to the reaction centre in the substrate, nucleophile, solvent, temperature). Stereospecificity in substitution reactions S_N1 mechanism non-stereospecific S_N2 mechanism stereospecific For example, tertiary centres react almost exclusively by the S_N1 mechanism whereas primary centres (except neopentyl centres) react almost exclusively by the S_N2 mechanism. When a nucleophilic substitution results in incomplete inversion, it is because of a competition between the two mechanisms, as often occurs at secondary centres, or because of double inversion (as when iodide is the nucleophile). The addition of singlet carbenes to alkenes is stereospecific in that the geometry of the alkene is preserved in the product. For example, dibromocarbene and cis-2-butene yield cis-2,3-dimethyl-1,1-dibromocyclopropane, whereas the trans isomer exclusively yields the trans cyclopropane.[4] This addition remains stereospecific even if the starting alkene is not isomerically pure, as the products' stereochemistry will match the reactants'. The disrotatory ring closing reaction of conjugated trienes is stereospecific in that isomeric reactants will give isomeric products. For example, trans,cis,trans-2,4,6-octatriene gives cis-dimethylcyclohexadiene, whereas the trans,cis,cis reactant isomer gives the trans product and the trans,trans,trans reactant isomer does not react in this manner. See also Dynamic stereochemistry References ^ a b "Overlap Control of Carbanionoid Reactions. I. Stereospecificity in Alkaline Epoxidation." Zimmerman, H. E.; Singer, L.; Thyagarajan, B. S. J. Am. Chem. Soc., 1959, 81, 108-116. ^ a b Eliel, E., "Stereochemistry of Carbon Compound", McGraw-Hill, 1962 pp 434-436 ^ March, Jerry (1985). *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure* (3rd ed.). New York: Wiley, ISBN 0-471-85472-7 ^ Skell, P.S. & Garner, A.Y. (1956). "The Stereochemistry of Carbene-Olefin Reactions. Reactions of Dibromocarbene with the cis- and trans-2-Butenes". *Journal of the American Chemical Society*, 78 (14): 3409-3411. doi:10.1021/ja01595a040. Retrieved from " 1 Stereoselective and Stereospecific Reactions 2 Stereoselective Reactions Many reactions can produce two or more stereoisomeric products. If a reaction shows a preference for one of the stereoisomers, it is stereoselective Stereoselectivity is intimately related to the mechanism of the reaction. 3 Examples of Stereoselective Reactions 4 Examples of Stereoselective Reactions 5 Examples of Stereoselective Reactions 6 H. W. Thompson, J. Org. Chem., 36, 2577 (1971).H. W. Thompson, E. McPherson, and B. L. Lences, J. Org. Chem., 41, 2903 (1976). 7 8 9 10 Hydride Reduction of Cyclic KetonesThe chair conformation of cyclohexanone places the carbonyl group in an unsymmetrical environment. The axial face has C(2)–H_{eq} bonds that are nearly eclipsed with the C=O bond and the C(3,5)-diaxial hydrogens point toward the trajectory for reagent approach. The equatorial face has axial C–H bonds at an angle of roughly 120 to the carbonyl plane. There is more steric bulk, including the 3,5-axial hydrogens, on the axial face. It is observed that small nucleophiles prefer to approach the carbonyl group of cyclohexanone from the axial direction, even though this is a more sterically congested approach. 11 Hydride Reduction of Cyclic KetonesTorsional effects are believed to play a major role in the preference for axial approach. In the reactant conformation, the carbonyl group is almost eclipsed by the equatorial C(2) and C(6) C–H bonds. This torsional strain is relieved by axial attack, whereas equatorial approach increases strain because the oxygen atom must move through a fully eclipsed arrangement. More bulky reducing agents usually approach the cyclohexanone carbonyl from the equatorial direction. This is called steric approach control and is the result of van der Waals repulsions with the 3,5-axial hydrogens. 12 Hydride Reduction of Cyclic Ketones 13 14 Stereospecific ReactionsSome reactions are stereospecific, that is reactions in which stereoisomeric reactants each provide stereoisomeric products. For example, the S_N2 substitution reaction results in an inversion of the configuration. It is a stereospecific reaction. The R-reactant gives the S-product and the S-reactant gives the R-product 15 Bromination of AlkenesThe addition of bromine is usually stereospecifically anti for unconjugated disubstituted alkenes and therefore the Z- and E-alkenes lead to diastereomeric products. 16 Bromination of Alkenes 17 Epoxidation and Dihydroxylation of AlkenesAn example of syn addition is osmium tetroxide- catalyzed dihydroxylation. This reaction is carried out using a catalytic amount of OsO₄, under conditions where it is reoxidized by a stoichiometric oxidant. The most common oxidants are t-butyl hydroperoxide, potassium ferricyanide, or an amine oxide. The two oxygens are added from the same side of the double bond. The key step in the reaction mechanism is a 3+2 cycloaddition that ensures the syn addition. 18 Epoxidation and Dihydroxylation of AlkenesAlkenes can be converted to diols with overall anti addition by a two-step sequence involving epoxidation and hydrolysis. The epoxidation is a syn addition that occurs as a single step. When epoxidation is followed by hydrolytic ring opening, the configuration of the diols is determined by the configuration of the alkene, usually with net anti dihydroxylation. The hydrolysis reaction proceeds by back-side epoxide ring opening. 19 20 Hydroboration-Oxidation HydroborationHydroboration-Oxidation Hydroboration is a stereospecific syn addition. The reaction occurs by an electrophilic attack by borane or alkylborane on the double bond with a concerted shift of hydrogen. Definition noun Relate to the specific points along the chain of configurations resulting in the spatial arrangement of atom in a polymer to create simple stereoisomer. Supplement Produces in a stereochemically specific processes thus, having crystalline properties like synthetic natural rubber (cis-polyisoprene). Demonstrate distinct specificity of one of several stereoisomers of reactants of the said enzymes for organic reactions. The value of stereospecificity is focus on the reactants and stereochemistry which is concerned with the products as long as it presents confirmation of a disparity in measures between stereoisomeric reactants that act on its own specific way. A stereospecific method denotes the stereochemical result of a specified reactant, while a stereoselective method chooses products that are available on a given reactant. In a single component, a stereospecific means will provide 100% of a particular stereoisomer though loss of stereochemical reliability can basically happen through opposing means with different stereochemical result. For example in nucleophilic substitution at sp³ at the center which can carry on by the stereospecific system that will result through inversion or non-specific mechanism which explain a simple selectivity for inversion depending on the reactants and the condition of the reactants that affected by some factors like temperature, solvent and substrate. If the substitution resulted in incomplete inversion it is because in the mechanisms at the center or double inversion. Compare: • stereoselective See also: • dynamic stereochemistry Related terms: • stereospecific (adjective) • stereospecifically (adverb) This tutorial elaborates on the effect of light on plant growth. It describes how different plants require different amo.. Proteins have a crucial role in various biological activities. Get to know how proteins are able to perform as enzymes, .. This tutorial noted some of the physical and chemical factors that provide the framework of a running water community in.. This tutorial presents the benefits and the possible adverse eventualities of genetic engineering. Know more about this .. This tutorial describes the sigmoid curve, annual plant growth, tree growth, human growth, and insect growth as the grow.. Find out more about New Zealand's unique biodiversity by exploring a range of different ecosystems and the key role of s.. Consider these E2 elimination reactions. For both, the β hydrogens are on the right side of the Br, and as expected, that's where the double bond appears in the product.So, no problems with the regiochemistry of these reactions. However, the stereochemistry is a different story. While the first reaction gives the E alkene as the major product, the Z alkene predominates in the second reaction. It is surprising since, remember, E alkenes are more stable because of sterical strain in Z alkenes.And the question is why and how one additional methyl group affected the stereochemical outcome of the reaction. Here is the short answer but we'll go over it in detail:Stereoselectivity of E2 reactionsThis all is explained by the geometrical requirement of the leaving group and the β hydrogen in the E2 mechanism. The transition state of the E2 mechanism requires an antiperiplanar orientation of the leaving group and the β hydrogen. Simply put, they need to be at 180°. Let's check this by using Newman projections and sawhorse representations, whichever works for you the best. We will be looking through the C1-C2 bond where the leaving group and the β hydrogens are:Using the Ha was one option which gave the expected E alkene. However, if we rotate around the C1-C2 single bond, it will be possible to align the Hb at 180° with the Br as well:So the elimination can occur from both conformations of the substrate since there are two β hydrogens. This is a stereoselective elimination - the molecule "selects" which β hydrogen to use to produce the most stable alkene (E is more stable than Z). Stereospecificity of E2 reactionsNow, let's draw the Newman projection of the second substrate:In this case, there's only one β hydrogen and therefore only one confirmation that allows to put it at 180° with the Br. It is not the most stable conformation, but the molecule has no choice as that is a requirement. Therefore, this is a stereospecific reaction.So, to determine whether it is a stereoselective or stereospecific E2 reaction, check the number of beta hydrogens:If there are two β hydrogens, it is stereoselective.If there is only one β hydrogen, it is stereospecific.It is worth to mention that not all stereospecific E2 reactions give the Z alkene. It depends on the stereochemistry of the substrate and as long as the β hydrogen is aligned antiperiplanar to the leaving group, the corresponding alkene will be formed (E or Z) A shortcut to stereospecific E2 reactionsPredicting the product of a stereospecific E2 reaction by drawing Newman projections is great for explaining the concept, yet time-consuming. So, let me give you a quick tip.To quickly predict the correct stereoisomer of a stereospecific E2 reaction check the wedge and dash of the beta hydrogen and the leaving group:if one is a wedge and the other one is dash, then it is good to go - simply erase them and place a double bond between these two carbons in the corresponding alkene.If there are cis (wedge-wedge or dash-dash), you need to flip the groups on the β carbon. As a result, the alkene does not have the configuration as predicted from the zig-zag structure of the substrate: 1.Identify the products and draw the curved-arrow mechanism for each of the following stereospecific E2 reaction: Drawing Newman projections to achieve the correct anti-periplanar conformation will be helpful. The key difference between stereospecific and stereoselective reactions is that, in stereospecific reactions, different stereospecific reactants give different stereoisomer of the product under ideal conditions (product is specific to the stereoisomer of the reactant), whereas in stereoselective reactions, a single reactant may give different types of stereoisomers. Stereochemistry is the part of chemistry that deals with the three-dimensional structures of the molecules. Stereochemical reactions are classified into two groups as stereospecific and stereoselective, based on the stereochemistry of the product. These products are called stereoisomers. CONTENTS 1. Overview and Key Difference 2. What are Stereospecific Reactions 3. What are Stereoselective Reactions 4. Side by Side Comparison - Stereospecific vs Stereoselective Reactions in Tabular Form 5. Summary What are Stereospecific Reactions? In a stereospecific reaction, each stereoisomeric reactant produces a different stereoisomeric product or a different set of stereoisomeric products. All stereospecific reactions are essentially stereoselective, but stereoselective reactions are not certainly stereospecific. Examples of stereospecific reactions include trans-addition of bromine to (E)- and (Z) alkenes, electrocyclic reactions like disrotatory ring closures, chelotropic syn-addition of singlet carbenes to alkenes, and the sigmatropic Claisen rearrangement of the cis- and trans- isomers of (4S)-vinylcyclopent-2-enes. Relationship All stereospecific reactions are essentially stereoselective. All stereoselective reactions are not essentially stereospecific. Examples trans-addition of bromine to (E)- and (Z) alkenes, electrocyclic reactions like disrotatory ring closures, chelotropic syn-addition of singlet carbenes to alkenes, and the sigmatropic Claisen rearrangement of the cis- and trans- isomers of (4S)-vinylcyclopent-2-enes diastereoselective reduction of 4-tert-butylcyclohexanone with lithium aluminum hydride, and enantioselective alkylation of benzaldehyde with organozinc reagents in the presence of (1R, 2S)-N,N-dibutylnorephedrine as the catalyst. What is the Difference Between Stereospecific and Stereoselective Reactions? Each stereoisomeric reactant produces a different stereoisomeric product or a different set of stereoisomeric products. A single reactant gives two or more stereoisomeric products, and one product is more prominent than the other product or products. Relationship All stereospecific reactions are essentially stereoselective. All stereoselective reactions are not essentially stereospecific. Examples trans-addition of bromine to (E)- and (Z) alkenes, electrocyclic reactions like disrotatory ring closures, chelotropic syn-addition of singlet carbenes to alkenes, and the sigmatropic Claisen rearrangement of the cis- and trans- isomers of (4S)-vinylcyclopent-2-enes diastereoselective reduction of 4-tert-butylcyclohexanone with lithium aluminum hydride, and enantioselective alkylation of benzaldehyde with organozinc reagents in the presence of (1R, 2S)-N,N-dibutylnorephedrine as the catalyst The terms of stereoselective and stereospecific reactions are assigned by observing the 3D structure of the stereoisomers in stereochemical reactions. In stereospecific reactions, each stereoisomeric reactant produces a different stereoisomeric product, whereas, in stereoselective reactions, a single reactant can produce two or more different stereoisomeric products. This is the difference between stereospecific and stereoselective reactions. Reference: 1. 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