Nucleophilic addition reaction pdf

Chapter 17: Aldehydes and Ketones. Nucleophilic Supplement to Nucleophil Supplement Nucleophilic Supplement Additions are an important class of reactions that allow the interconversion of CSO into a number of important functional groups. What does the term nucleophilic supplement mean? Nucleophile, Nu-, is an electron-rich species that will react with an electron of poor species (here C'O) Adding implies that the two systems merge into one entity. There are three fundamental events in the nucleophilic reaction of addition: the formation of a new link between nucleophilic, Nu, to the electrophilic C group C'O breaking p communication with O as a result of the formation of intermediate protonoxide alkoxide alkoxide to give a derivative alcohol Depending on the nucleophilic reaction, there are two possible common scenarios: Strong nucleophils (Ayon) add directly to the C'o Aloxidees were then protoned at work with diluted acid. Examples of such nucleophilic systems are: RMgX, RLi, RC≡CM, $LiAlH_4$, $NaBH_4$ Weak Nucleophils (neutral) require that C'O be activated before the Nu attack. This can be done using an acid catalyst that protons onto Lewis Main O and makes the system more electrophilic. Examples of such nucleophilic systems are: H_2O, ROH, $R\text{-}NH_2$ Protonation carbonyl gives a structure that can be repained in another resonant form, which shows the electrophilic nature of C, as it is carbocing. Reactions on the following pages are catalogued based on the nature of the nucleophilic atom. In most cases, the mechanism is useful indentify in each case in terms of the two common schemes presented above. © Dr. Ian Hunt, Department of Chemistry Illustrated Glossary organic chemistry nucleophil reaction adding a chemical supplement in which nucleophilic forms of sigma bond with electron-deficient species. These reactions are considered very important in organic chemistry because they allow the conversion of carbonyl groups into different functional groups. Typically, nucleophil reactions adding carbonyl compounds can be broken down into the next three steps. Electrophilic carbonyl carbonate carbonus form a sigma connection with a nucleophilic. The link between carbon and oxygen is currently broken, forming an intermediate alkoxide (the connection of a pair of electrons is transmitted to the oxygen atom). Subsequent protonation of aloxide gives a derivative of alcohol. The double bond between carbon and oxygen is directly attacked by strong nucleophils to cause alcoxide. However, when weak nucleophils are used, the carbonyl group must be activated using an acid catalyst for the nucleophilic reaction of adding to proceed. Teh The group has a coplanar structure and its carbon sp^2 is hybridized. However, the nucleophil attack on the CSO group leads to a rupture of the wee link. Carbonyl carbon dioxide is currently sp^3 hybridized and forms a sigma link with the nucleophil. The resulting alcoxide intermediate has tetraetric geometry, as shown above. Why do carbonyl compounds undergo nucleophilic supplement? In carbonyl compounds, the link between carbon and oxygen is polar. Because of the relatively higher electronegatity of the oxygen atom, the electron density is higher near the oxygen atom. This results in the generation of a partial negative charge on the oxygen atom and a partial positive charge on the carbon atom. Since carbonyl carbon has a partial positive charge, it behaves like an electrophile. A partial negative charge on an oxygen atom can be stabilized by introducing an acidic group. A proton donated by acid bonds with a carbonyl oxygen atom neutralizes the negative charge. Aldehydes are relatively more reactive to nucleophil reactions added compared to ketones. This is due to the fact that secondary carboceses formed by ketones are stabilized by neighboring groups R. Primary carboceses formed by aldehydes are less stable than secondary carboceses formed by ketones, and therefore more susceptible to nucleophilic attacks. Reactions with hydrogen cyanide Nucleophil reaction adding between hydrogen cyanide (HCN) and carbonyl compounds (usually aldehydes and ketones) leads to the formation of cyanohydrins. Basic catalysts are often used to increase the speed of reaction. Cyanide anion (CN-) acts as a powerful nucleophil and attacks carbonyl carbonic carbon to form a new sigma bond, as shown below. The polar nature of the CSO communication makes carbon carbon electrophilic in nature. Cyanide anion performs a nucleophilic attack on carbon dioxide, causing the formation of intermediate. This intermediate is being protoned to afford the product of cyanogdrin. Nucleophilic supplements with monohydrol alcohols Aldehydes and ketones undergo nucleophilic reactions added with monohydrol alcohols to give hemiacetals. With further reaction with another alcohol molecule, acetal is produced. Since alcohols are weak nucleophils, the reaction requires an acid catalyst to activate the carbonyl group to the nucleophilic attack. Since heiacetals can be exposed to hydrolysis to give a reaction (alcohol and carbonyl compounds), the water generated during the reaction must be removed. In this reaction, carbonyl oxygen is protoned until a nucleophilic attack is carried out by alcohol. Nuclear alcohol is being deprotoned to form hemacet. This reaction can be repeated to get acetal. Other Nucleophilic Adding with Grignard Reagents Reagents Grignard (general formula: R-Mg-X) attributes a partial negative charge to the carbon atom. The following types of alcohol are formed from nucleophil reactions added with Grignard reagents. Primary alcohols are formed with formaldehyde. Other aldehydes give secondary alcohols when reacting with Grignard reagents. Nucleophilic reactions between ketones and Grignard reagents give tertiary alcohols. The overall mechanism of these reactions involves attacking nucleophilic carbon (owned by R-Mg-X) on carbonyl carbon dioxide. The simple acidic work of the resulting alcoxic gives the appropriate alcohol. The reaction with primary amines Reaction between primary amines and aldehydes/ketones gives derivatives of imin along with water. The reaction can be illustrated as follows. Initially, nucleophilic nitrogen belonging to amine attacks carbonyl carbon. The dual link between carbon and oxygen is broken, and a new link between carbon and nitrogen sigma is formed. The proton is now transported from the amin to the oxygen atom. At the next stage of this nucleophilic supplemention reaction, the OH group is further protoned and the water is removed. The carbon atom now forms a double bond with nitrogen belonging to the amine. This nitrogen is being deprotoned to afford the necessary imine product. To learn more about add-on nucleophilic reactions and other related concepts such as SN1 reactions, sign up for BYJU'S and download the mobile app to your smartphone. Goals After completing this section, you should be able to give a general description of the nucleophilic reactions of adding aldehydes and ketones, revealing two possible courses (or variations) that such reactions may take after the initial nucleophilic attack. explain why aldehydes tend to undergo nucleophil reactions adding more easily than ketones, and determine which of the two aldehydes or ketones data will react most easily in such reactions. Key terms make sure you can define and use in the context of the key term below. Nucleophil Reactions Adding Insights Notes We've already discussed electrophilic reactions adding to some length; Now you will meet the nucleophil reactions of the addition for the first time. The nucleophilic reactions of the addition include the initial attack of the nucleophil on the slightly positive carbon center of the carbon group carbonyl. Before we take a detailed look at the reactivity of aldehydes and ketones, we need to look back and remind ourselves of what the carbonyl bond pattern looks like. Carbonyl carbonates sp^2 are hybridized, with three sp^2 orbits forming soverlaps with orbits on oxygen and on two carbon or hydrogen atoms. These three connections take three-goonic planning geometry. The remaining non-hybrid 2p orbital on the central carbonyl carbonic carbon is perpendicular to this side by side pbond with 2p orbital on oxygen. The dual bond between carbon and oxygen is polar: oxygen is more electronegic than carbon, so the density of electrons is higher on the oxygen side of the connection and lower on the carbon side. Recall that the polarity of the communication can be depicted with a dipole arrow, or by showing oxygen as holding a partial negative charge and carbonyl carbonyl of carbon monoxide partial positive charge. The third way to illustrate the carbon-oxygen dipole is to consider the two main resonant contributors of the carbonyl group: the basic form, which is what you usually see drawn in Lewis's structures, and a minor but very important contribution in which both electrons in pbond are localized to oxygen, giving it a complete negative charge. The last image shows carbon with an empty 2p orbit and a full positive charge. The result of polarization of carbonyl bonds, no matter how it is portrayed, is simply to predict. Carbon, because it is poor with an electron, is an electrophile: it is an excellent target for attack by an electron-rich nucleophilic group. Since the oxygen end of the dual carbonyl bond carries a partial negative charge, anything that can help stabilize this charge by adopting a portion of the density of electrons will increase the polarity of the connection and make the carbon more electrophilic. Very often the general acid group serves this purpose by donating proton carbonyl oxygen. The same effect can be achieved if Lewis' acid, such as magnesium ion, is near carbonic oxygen. Unlike in the situation in the nucleophil substitution reaction, when the nucleophilia attacks aldehyde or carbon ketone there is no leaving group - the incoming nucleophil simply pushes the electrons into the wee bonding to oxygen. Also, if you start with a minor resonant contributor, you can imagine it as a nucleophil attack on carbocing. After carbonyl is attacked by nucleophil, negatively charged oxygen is able to act as a nucleophil. However, most often oxygen acts instead as a basis, abstracting the proton from a nearby acid group into a solvent or enzyme active site. This very common type of reaction is called nucleophilic supplement. This second brew of the common nucleophilic addition of carbonyl oxygen is completely removed as water from the C'Nu connection. In general, aldehydes are more reactive than ketones due to the lack of a stabilizing alcley group. Primary carboconation, formed in the polarizing resonant structure of aldehyde (discussed above), is less stable and therefore more reactive than the secondary carbocon, formed by ketone. 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