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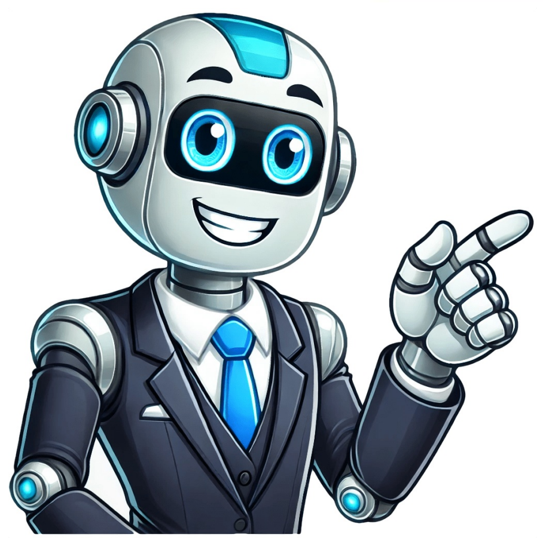

Acid chlorides which are also known as acyl chlorides are organic compounds that contain a carbonyl group (C=O) bonded to a chlorine atom. They are derived from carboxylic acids by replacing the hydroxyl group (-OH) with a chlorine atom. Acid chlorides are highly reactive and serve as important intermediates in organic synthesis.1.0General Structure and Nomenclature of Acid ChlorideThe general formula for acid chlorides is RCOCl, where:R is an alkyl or aryl group.CO represents the carbonyl group (C=O).Cl is the chlorine atom attached to the carbonyl carbon.Nomenclature and Common names of Acid ChloridesThe IUPAC name for acid chlorides is derived from the corresponding carboxylic acid by replacing the suffix "-ic acid" or "-oic acid" with "-yl chloride".Example: Ethanoyl chloride is named after ethanoic acid (acetic acid), and benzoyl chloride is derived from benzoic acid.Common Names:Acid chlorides are often named based on their parent carboxylic acid.CH_3COCl is acetyl chloride (from acetic acid).C_6H_5COCl is benzoyl chloride (from benzoic acid).2.0General Properties of Acid ChloridePhysical Properties of Acid Chlorides:Chemical Properties of Acid ChlorideAcid chlorides react vigorously with water to form carboxylic acids and hydrochloric acid (HCl). The nucleophilic water molecule attacks the electrophilic carbonyl carbon, leading to the release of HCl.RCOCl + H2O → RCOOH + HClReaction with Alcohols (Formation of Esters): Acid chlorides react with alcohols in the presence of a base like pyridine to form esters.RCOCl + R′OH → RCOOR′ + HClExample: Acetyl chloride reacts with ethanol to form ethyl acetate.Reaction with Ammonia and Amines (Formation of Amides): Acid chlorides react with ammonia or amines to form primary, secondary, or tertiary amides.RCOCl + NH3 → RCONH2 + HClExample: Benzoyl chloride reacts with ammonia to form benzamide.Reaction: Acid chlorides react with aromatic compounds in the presence of a Lewis acid catalyst like aluminum chloride ($AlCl_3$) to form aryl ketones.RCOCl+C6H6AlCl3RCOC6H5 +HClExample: Acetyl chloride reacts with benzene to form acetophenone.Reaction with Grignard Reagents (Formation of Ketones or Tertiary Alcohols): Acid chlorides react with Grignard reagents to form ketones or tertiary alcohols depending on the amount of Grignard reagent used.RCOCl + RMgX → RCOOR′Example: Acetyl chloride reacts with methylmagnesium bromide to form acetone.Reduction to Aldehydes and AlcoholsAcid chlorides can be reduced to aldehydes using lithium tri-tert-butoxyaluminum hydride or to alcohols using lithium aluminium hydride ($LiAlH_4$).RCOCl + 2[H] → RCHO + HClRCOCl + 4[H] → RCH2OH + HClReaction with Lithium Dialkyl Cuprates (Gilman Reagent)Acid chlorides react with lithium dialkyl cuprates to form ketones.RCOCl + (R′)2CuLi → RCOR′ + R′Cu + LiClHere is a summary of the Chemical Reactions of Acid chlorides3.0Preparation of Acid ChloridesAcid chlorides are commonly prepared by reacting a carboxylic acid with thionyl chloride ($SOCl_2$), phosphorus trichloride (PCl_3), or phosphorus pentachloride (PCl_5). RCOOH + SOCl2 → RCOCl + SO2 + HClFrom Esters: Acid chlorides can be synthesized by treating esters with phosphorus pentachloride (PCl_5). In this tutorial we're going to go over the acid chlorides (acyl chlorides), their synthesis, and common reactions of acid chlorides you're likely going to see in your homework or on the test. First of all, what exactly are the acid chlorides? Acid chlorides, or acyl chlorides, are derivatives of carboxylic acids that have a chlorine atom directly attached to the carbonyl group. Due to the polarization of the carbonyl and inductive effect of the chlorine atom, acid chlorides are quite electrophilic and are extremely reactive towards nucleophiles. While there are a lot of possible reactions of acid chlorides, here I'm going to only focus on the most common ones that are typically covered in a sophomore organic chemistry course. Before we can look at the reactions of acid chlorides, it's a good idea to first look at how exactly we make them. There are two typical reactions you're going to see that yield acid chlorides: Reaction of carboxylic acids with thionyl chloride, Reaction of carboxylic acids with PCl3 or PCl5. The reaction with thionyl chloride is more common, so let's look at it first. Mechanistically speaking, this reaction is a somewhat typical acyl substitution. The first part of the mechanism modifies the carboxylic acid so that we have a good leaving group. Once we have a good leaving group on the carbonyl, we can do the acyl substitution reaction making the acid chloride. Importantly, the co-products in this reaction are either gaseous or are bound by pyridine if we choose to use that as a solvent. The use of pyridine here is completely unnecessary. However, we often see it in the textbooks and it's likely your instructor is going to give you this reaction with pyridine as a solvent. The second method uses phosphorous tri- or pentachloride. This reaction is based on the same principle as the former one — we make a good leaving group and kick it out. Mechanistically, this reaction starts in a similar way to the former reaction with thionyl chloride by using our reagent to modify the carboxylic acid. I'm only going to show the mechanism here for the phosphorous pentachloride, but the phosphorous trichlorde mechanism is functionally the same. The co-product here is unfortunately not a gas, so it's a little more difficult to isolate our product. Which method should you choose to use on the test? It doesn't matter. You may choose any. As I've mentioned a moment ago, the reaction with thionyl chloride is more common. So, chances are, your instructor didn't even show you the ones with phosphorous chlorides at all. Acid chlorides are among the most electrophilic derivatives of carboxylic acids. So, it's easy to convert acid chlorides into virtually any other carboxylic acid derivative by replacing the chlorine atom with the corresponding nucleophile. So, let's look at these reactions one by one from more electrophilic derivatives, to the less electrophilic ones. All these reactions will have the same general mechanism: The first step is always going to be a nucleophilic attack on the carbonyl of the acid chloride making a tetrahedral intermediate. Depending on the nature of your nucleophile, you might need a proton transfer. Then, we're going to have a leaving group dissociation giving us the final product. When acid chlorides react with carboxylic acids, they make the corresponding acid anhydrides. The reaction occurs very smoothly with either deprotonated version (carboxylate) or the neutral version of the carboxyl acid itself. As the result, you can make either symmetrical or non-symmetrical acid anhydrides. Some instructors like to make asymmetric anhydrides on the tests, even though they are not particularly useful for any purposes. When acid chlorides react with alcohols or alkoxides, they make corresponding esters. Typically, we perform this reaction with alcohols rather than alkoxides. Alkoxides are quite reactive and bringing them together with acid chlorides, which are also very reactive, make a very exothermic reaction which is hard to control. Plus, alkoxides are basic which may also result in unwanted side-reactions. When acid chlorides react with water or hydroxides, they make carboxylic acids. Like in the case of alkoxides, we typically don't do this reaction with hydroxides. Additionally, reaction with hydroxides results in deprotonation of the carboxylic acid making a carboxylate (salt) with whatever base we're using. Reaction of acid chlorides with amines results in the formation of the amides. This reaction requires either two equivalents of the amine or a sacrificial base that is required to neutralize hydrochloric acid (co-product in this reaction). As a "sacrificial base" we typically use either triethylamine or pyridine. This becomes necessary if your amine is very expensive and you can't afford to just waste one equivalent of the reagent. Acid chlorides react with organometallic compounds like organolithium compounds, Grignard reagents, and organocuprates (Gilman reagent) giving alcohols or carbonyls depending on the reaction conditions and the nature of the organometallic compound. Organolithium compounds and the Grignard reagents react with acid chlorides in a similar fashion. The reaction typically goes through two rounds of addition. However, as the intermediate in this reaction — ketone — is less reactive than the acid chloride, it is possible to neatly control your reaction and only perform a single addition. This can only be done if we add the organometallic reagent to our acid chloride to make sure that the chloride is always in excess. But even then, the reaction tends to be less and less controllable as we consume the acid chloride and make more and more ketone. So, unless your instructor specifically points out that this is ok for your class, always do the addition twice like in the first example I showed you here. Is it possible to make sure we stop at the formation of the ketone though? Yes! Gilman reagents (organocuprates) do not react with ketones making it possible to stop the reaction at the formation of the ketone. So, if you want to make sure that you only do a single addition of your organometallic reagent to the acid chloride, use the organocuprates. Complex hydrides are excellent sources of nucleophilic hydride ions. Since acid chlorides are very electrophilic, they easily react with all common complex hydrides like lithium aluminum hydride or sodium borohydride. An important thing to remember here is that these reactions will always give you a complete reduction all the way to the corresponding primary alcohols. Mechanistically speaking, the reaction is just a series of the nucleophilic attacks on the carbonyl. And as the hydrides are intrinsically basic, we are always going to end up with the alkoxide as the product. So, we need to make sure we do the acidic workup at the end to neutralize (protonate) the alkoxide. Interestingly enough, but if you use a very bulky complex hydride at a very low temperature, you can reduce the acid chloride to an aldehyde and not an alcohol. The most common examples of such bulky complex hydrides are lithium tris-tert-butoxy aluminum hydride and diisobutylaluminum hydride (DIBAL). A low temperature here is essential. If the temperature is not low enough, the bulky hydrides are going to act just like the regular hydrides and reduce your acid chloride all the way to the primary alcohol. Download the Testbook APP & Get Pass Pro Max FREE for 7 Days10,000+ Study NotesRealtime Doubt Support71000+ Mock TestsRankers Test Series+ more benefitsDownload App Now Acid chloride has the molecular formula RCOCl, where R is a side chain. They are carboxylic acid reactive derivatives. An acyl chloride (or acid chloride) is an organic compound composed of a chlorine atom attached to an acyl group in organic chemistry. An acyl group is a functional group defined by the molecular formula of RCO. Thus, the acid chloride family is part of a larger organic family known as acyl halides. Table of Contents Formation of Acid Chlorides Laboratory method Acid chlorides are formed when carboxylic acids react with thionyl chloride (SOCl2). The carboxylic acid's hydroxyl group is converted to a chlorosulfite intermediate during the reaction, making it a better leaving group. The chloride anion formed as a result of the reaction acts as a nucleophile. Industrial Method Acetic anhydride is reacted with hydrogen chloride to produce acetyl chloride in the industrial process. (CH3CO)2O + HCl → CH3COCl + CH3CO2H Certain phosphorus chloride reagents, such as phosphorus trichloride or phosphorus pentachloride, can also be used to prepare acyl chlorides: RCOOH + PCl5 → RCOCl + POCl3 + HCl Naming Acid Chlorides Acyl chlorides are named by taking the name of the parent carboxylic acid and substituting -yl chloride for -ic acid where the acyl chloride substituent takes priority. Thus: Carboxylic acid name Acyl chloride name Acyl chloride formula ethanoic acid ethanoyl chloride CH3COCl propanoic acid propanoyl chloride CH3CH2COCl butanoic acid butanoyl chloride CH3CH2CH2COCl When other functional groups predominate, acyl chlorides are referred to as prefixes- chlorocarbonyl. For example- ClOCCH2COOH is named as (chlorocarbonyl)acetic acid Physical Properties 1. Appearance- Lower acyl chlorides are colourless liquids with a strong odour. 2. Solubility- They dissolve in organic solvents like alcohol, ether, and chloroform. 3. Boiling points and Melting points- The boiling points and melting points of acyl chlorides are lower than those of the corresponding acids which is due to the lack of ability to form hydrogen bonds. Chemical Properties and Reactions Due to their high reactivity, acid halides can be easily converted into other acyl compounds via nucleophilic acyl substitution. 1. They are the most reactive of all carboxylic acid derivatives. 2. Through nucleophilic acyl substitution, acid chlorides react with carboxylic acids to form anhydrides. 3. Acyl chlorides can be easily hydrolyzed by water to produce the corresponding carboxylic acids. 4. Esters are formed when acid chlorides react with alcohol nucleophiles. This is the preferred method for producing esters. To remove the HCl produced, pyridine is frequently added to the reaction mixture. 5. Primary alcohols are produced by reducing acyl chlorides with lithium aluminium hydride and di-isobutyl aluminium hydride. 6. In the presence of palladium, they are reduced by hydrogen with BaSO4 to an aldehyde. This reaction is the Rosenmund Reaction. 7. Ammonia, 1° amines, and 2° amines react with acid chlorides to form 1°, 2°, and 3° amides respectively. 8. When Grignard reagents are added, acid halides are converted to 3° alcohols. During this reaction, the Grignard reagent adds to the carbonyl carbon twice. 9. When an acid chloride is reacted with a diorgano cuprate (Gillman) reagent (R2CuLi), an excellent yield of ketone product is produced. Hazards Since acyl chlorides are such reactive compounds, they are generally toxic and should be handled with extreme caution. They are lachrymatory chemicals because they can react with water on the eye's surface, producing hydrochloric and organic acids that are irritating to the eye. Inhaling acyl chloride vapours can cause similar problems. Uses of Acid chlorides Acid chlorides are reactive chemical species by nature, and they are used as key building blocks in a wide range of downstream applications. Some of the uses are as follows- Reagents for chemistry Pharmaceutical manufacturing Synthesis of organic compounds Peroxides of organic origin Production of agrochemicals Pigments and plastics Acid chlorides are formed when carboxylic acids react with thionyl chloride (SOCl2). The carboxylic acid's hydroxyl group is converted to a chlorosulfite intermediate during the reaction, making it a better leaving group. The chloride anion formed during the reaction functions as a nucleophile. Some examples of acid chlorides are ethanoyl chloride- CH3COCl, propanoyl chloride- C2H5COCl, butanoyl chloride- C3H7COCl, benzoyl chloride, etc. Acyl chlorides are generally toxic, and special precautions must be taken when handling them. They can react with water on the eye's surface, producing hydrochloric and organic acids that causes irritation to the eye. Since there is no H+ to donate, anhydrous acid chloride is neutral. However, in an aqueous medium, acid chloride can react with water to form carboxylic acid and HCl. Since acyl chlorides have a good leaving group attached to the carbonyl carbon, they are more reactive than carboxylic acids or carboxylic esters. Put your understanding of this concept to test by answering a few MCQs. Click Start Quiz to begin! Select the correct answer and click on the "Finish" buttonCheck your score and answers at the end of the quiz Visit BYJU'S for all Chemistry related queries and study materials 0 out of 0 arewrong 0 out of 0 are correct 0 out of 0 are Unattempted View Quiz Answers and Analysis The traditional methods utilize sulfur or phosphorous halides to convert the acid to the acid chloride. ACID CHLORIDES Traditional textbook preparations of acid chlorides from carboxylic acids include The traditional methods utilize sulfur or phosphorous halides to convert the acid to the acid chloride. Of these methods, thionyl chloride [often with a catalytic amount of dimethyl formamide (DMF)] is the most useful since the by-products of the reaction are gases (SO2, HCl) which can be easily purged from the reaction mixture with a stream of nitrogen. The acid chloride product can then be purified on a small scale by bulb-to-bulb distillation or crystallization. Because an excess of thionyl chloride is usually used, there must be a purification step to remove the excess reagent. Another superior reagent for the preparation of acid chlorides is oxallyl chlo-ride in methylene chloride. Addition of a carboxylic acid leads to the smooth evolution of gas (CO2, CO, HCl) which can be used as a crude monitor of the reaction progress. The acid chloride is very easily purified since oxallyl chloride boils at 62◦ C and is easily evaporated from the product. In many instances, the crude product is sufficiently pure to be used directly. Replacing the -OH group using phosphorus(V) chloride, PCl5 Phosphorus(V) chloride is a solid which reacts with carboxylic acids in the cold to give steamy acidic fumes of hydrogen chloride. It leaves a liquid mixture of the acyl chloride and a phosphorus compound, phosphorus trichloride oxide (phosphorus oxychloride) - POCl3. The acyl chloride can be separated by fractional distillation. For example: Replacing the -OH group using phosphorus(III) chloride, PCl3 Phosphorus(III) chloride is a liquid at room temperature. Its reaction with a carboxylic acid is less dramatic than that of phosphorus(V) chloride because there is no hydrogen chloride produced. You end up with a mixture of the acyl chloride and phosphoric(III) acid (old names: phosphorous acid or orthophosphorous acid), H3PO3. For example: Again, the ethanoyl chloride can be separated by fractional distillation. Replacing the -OH group using sulphur dichloride oxide (thionyl chloride) Sulphur dichloride oxide (thionyl chloride) is a liquid at room temperature and has the formula SOCl2. Traditionally, the formula is written as shown, despite the fact that the modern name writes the chlorine before the oxygen (alphabetical order). The sulphur dichloride oxide reacts with carboxylic acids to produce an acyl chloride, and sulphur dioxide and hydrogen chloride gases are given off. For example: The separation is simplified to an extent because the by-products are both gases. You would obviously still have to fractionally distil the mixture to separate the acyl chloride from any excess acid or sulphur dichloride oxide. © Jim Clark 2004 (modified December 2015) Resonance is one of those topics in organic chemistry that can trip up students, but it's absolutely crucial for understanding how molecules behave. I have already talked about the resonance structures in another tutorial. If you haven't worked through that one yet, di it first before looking at the material here. In this tutorial, I'll go over the most common questions students have about resonance and pay close attention to the major and minor resonance contributors. So, let's break it down step by step and answer some common questions that often come up. Resonance helps us understand how electrons are distributed in a molecule. In many cases, a single Lewis structure can't fully capture what's happening with the electrons. So, resonance gives us a way to represent the true electron distribution as a hybrid of multiple possible structures. This is key because it affects a molecule's stability, reactivity, and bond lengths. Essentially, resonance shows how delocalized electrons can make a molecule more stable and influence how it reacts with other molecules. This is where things can get confusing, but it's actually pretty simple once you get the hang of it. Resonance structures are different ways of drawing the arrangement of electrons (like lone pairs or pi bonds) in a molecule, while the atoms stay in the same positions. These structures are hypothetical—they don't exist on their own but help illustrate possible electron placements. The resonance hybrid, on the other hand, is the real deal. It's the true form of the molecule, which is an average or "blend" of all the resonance structures. The hybrid reflects the actual distribution of electrons, where they're spread out (delocalized) over several atoms, rather than being confined to one bond or location. Think of the hybrid as a "best fit" representation of the molecule, where the electrons are more spread out and the molecule is more stable as a result. You might wonder, "If the hybrid is closer to reality, why don't we just draw that?" Well, it's because the hybrid doesn't clearly show how electrons are shifting or delocalized. Resonance contributors, on the other hand, help us visualize specific electron movements, like lone pairs shifting or pi bonds relocating. This is useful for predicting how the molecule will react with others. By showing each resonance contributor, we can better understand the nature of electron delocalization, making it easier to predict a molecule's stability and reactivity. So, even though the hybrid is the real electron distribution, resonance contributors are the practical tool that gives us insight into how electrons are behaving. Nope! Not all resonance contributors are equally important. Some are more significant because they more closely resemble the true structure of the molecule. Here are a few rules to determine which contributors matter the most: Complete octets: The more atoms that have a full octet of electrons, the better. We especially pay attention to the atoms bearing charges. Carbocations: If we only have structures with carbocations, we'll typically prioritize the 3° position over the 2° and 1° Charge location: If a contributor has charges, negative charges are best on electronegative atoms like oxygen or nitrogen. Minimized formal charges: Contributors with fewer formal charges are more stable. Neutral molecules tend to be more significant. Aromatic Rings: Intact aromatic rings tend to make larger contribution to the overall hybrids than the "broken" aromatic rings that donated some of the electron density to make a resonance contributor. So, while having multiple resonance structures is good, the most important ones will follow these rules. These contributors make a bigger impact on the overall stability and properties of the molecule. Resonance isn't just about counting how many contributors a molecule has—it's about identifying the most stable and significant ones that help us understand how the electrons are really distributed. Once you get the hang of spotting the important resonance structures, the concept of resonance starts to make a lot more sense. It's all about understanding how delocalized electrons stabilize molecules and affect their behavior. This article serves as a guide to the acid chloride functional group in organic chemistry. After reading this article, you will be able to understand and describe the naming conventions of acid chlorides, how they are synthesized, the chemical reactions they undergo, and their uses and applications. The acid chloride (or acyl chloride) functional group in organic chemistry is derived from the carboxylic acid functional group. Known for their versatility and unique reactivity, acid chlorides are essential for various chemical reactions and industrial applications. It is also worth noting that acid chlorides are very similar to other common functional groups such as acid anhydrides, aldehydes, and ketones. For example, all of them contain a carbonyl group. However, properties such as reactivity are different due to the chlorine atom of acid chlorides. Chlorine is highly electronegative which makes the carbonyl carbon attached to the chlorine atom strongly positive. This means that acid chlorides are more open to nucleophilic attack and therefore more reactive than other carbonyl containing functional groups. Structure: Almost a carboxylic acid group, but with Cl instead of OH General formula: Acid chlorides have the general formula of RCOCl where R is a side chain. Acidity: Neutral for anhydrous acid chlorides since there are no H+ ions to donate. Solubility: Soluble in organic solvents such as alcohols and ethers but insoluble in water. IR Spectroscopy: Acid chlorides show a strong C=O band at 1775-1810 cm-1 and a C-Cl stretch from 550-730 cm-1. Acid chlorides are named based on the specific carboxylic acids that they are derived from. This is specifically done by substituting the -ic acid prefix of the parent carboxylic acid with -yl chloride. For example, the name of the acid chloride derived from butanoic acid would be butanonyl chloride. Basic rules for naming acid chlorides: Select the longest carbon chain to begin naming. Number from the carbonyl (C=O) carbon. Add the suffix of -yl chloride to the parent carbon chain name. Acid chlorides are most commonly prepared by reacting carboxylic acids with thionyl chloride (SOCl2). The hydroxyl group (OH) of the carboxylic acid is replaced with a chlorine atom (Cl) to form an acid chloride. The reaction mechanism starts with carboxylic acid acting as a nucleophile which attacks the thionyl chloride. Next, the chlorine atom (Cl) is removed as a leaving group which forms a chlorosulfite intermediate. The chlorine atom acts as leaving group and becomes a chloride anion (Cl–) that then performs a nucleophilic attack on the carbonyl group. This is then followed by the removal of the thionyl chloride as a leaving group. The final step is deprotonation which forms the acid chloride product and hydrochloric acid (HCl) as a byproduct. General Reaction Reaction Mechanism Additionally, it is worth noting that acid chlorides can also be prepared by reacting carboxylic acids with phosphorus chloride reagents such as phosphorus trichloride (PCl3) and phosphorus pentachloride (PCl5). Acid chlorides are highly reactive organic compounds and therefore readily undergo a variety of reactions such as nucleophilic acyl substitution, Friedel-Crafts acylation, and esterification. Nucleophilic acyl substitution can convert acid chlorides into many other acyl compounds such as carboxylic acids, esters, ketones, aldehydes, alcohols, amides, and acid anhydrides. Examples of nucleophiles that react with acid chlorides include water, alcohols/phenols, and ammonia/amines. The reaction mechanism for acid chloride nucleophilic acyl substitution involves nucleophilic attack, leaving group removal, and deprotonation. General reaction Reaction Mechanism General Reaction Reaction Mechanism General reaction Reaction Mechanism General Reaction Reaction Mechanism Acid chlorides react with benzene in Friedel-Craft acylation reactions. These reactions occur in the presence of an aluminum chloride catalyst (AlCl3) and result in the production of aromatic ketones, comprised of a phenyl group attached to a carbonyl group. This reaction is important in organic chemistry since it is an effective way to attach hydrocarbon groups to benzene. Similar to carboxylic acids, acid chlorides can undergo esterification reactions, reacting with alcohols to form esters. A significant difference is that esterification with the use of acid chlorides makes the reaction irreversible. The reaction mechanism for acid chloride esterification begins with nucleophilic addition where the alcohol acts as a nucleophile and attacks the carbonyl group of the acid chloride. This is then followed by elimination which involves leaving group removal and deprotonation. Nucleophilic addition Elimination In organic chemistry, acid chlorides have the general use of synthesizing other organic compounds, as previously mentioned. Acid chlorides have several valuable industrial applications due to their versatility as an organic reagent. Examples include the synthesis of pharmaceuticals, agrochemicals, fragrances, pigments, and plastics. This article serves as a guide to the acid chloride functional group in organic chemistry. 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