Reagent used to convert primary alcohol to aldehyde

Alcohols, Synthesis and Reactions Today, we'll examine the chemistry of alcohols. First, we'll review the reactions we've already seen which make alcohols. Then we'll look at the reactions of the alcohol functional group. Here's a list of reactions we've already seen which make alcohols. The links will take you back to a previous lecture where the specific reactions are discussed. The last reaction needs some further comment. Here's how we would do it: The mechanism is similar to the mechanism for the reduction of esters by LiAlH4, so we will not be concerned with the details. We can conclude that LiAlH4 can be used to make a primary alcohol from either an ester or the corresponding carboxylic acid. We can extend our understanding of the use of this reaction in synthesis by asking "How could we make the carboxylic acid we need for this reaction?" One particularly important way to do that, important because it makes a carbon-carbon bond, is to make a carboxylic acid by use of the addition of a Grignard reagent to carbon dioxide. This combination gives us a two step way to convert an alkyl halide (RBr) to a primary alcohol with the addition of one more carbon to the chain. Of course, this raises the question: "Where do we get the RBr?" That takes us into the reactions of alcohols, because the most effective way to make alkyl halides is from alcohols. If we wish to make alkyl bromides, there are two reactions to consider. If the alcohol is primary or secondary, the reagent of choice is phosphorous tribromide (PBr3). If the alcohol is tertiary, we use hydrogen bromide (HBr) to ake the alkyl halide. The situation is similar if we wish to make an alkyl chloride. HCl is used for tertiary alcohols and SOCl2 is used for primary and secondary alcohols. We'll take up the mechanisms of these reactions later. (If you wish to look ahead, see Chapter 7 in Brown.) We now have an answer to the question of how to make alkyl bromides, so we can add another reaction to the beginning of the sequence we started with: The alcohol product of this sequence can be used to make an alkyl halide to start a new sequence, which could be the starting point for a further sequence, etc. This makes alcohols extremely valuable synthetic reagents. Suppose we used an aldehyde or ketone instead of carbon dioxide in such a sequence: Here the product alcohol is produced directly rather than through a carboxylic acid. Notice that it is a secondary (from an aldehyde) or tertiary (from a ketone) alcohol, as we had seen when we looked at Grignard additions to aldehydes and ketones. Since this has shown that one of the important components in a Grignard addition can be made from an alcohol, it seems natural to wonder whether the other major component, the aldehyde or ketone can be made from an alcohol. (We won't worry about how to make carbon dioxide -- there's plenty of it around.) The answer is yes, we can make an aldehyde or a ketone from an alcohol. The desired transformation is: The products of these reactions have fewer hydrogens than the reactants, so these are oxidations. In the case of the ketone, further oxidation would require breaking a carbon-carbon bond to one of the R groups which is quite difficult. We can use chromic acid (K2Cr2O7 - H2SO4). The situation with the aldehyde is more difficult, since we already know that the use of chromic acid will oxidize it to a carboxylic acid. It took considerable research to work out, but the reagent which works here is called pyridinium chlorochromate (PCC for short). Our synthetic reactions for the oxidation of alcohols are then: We can add the above reactions to our growing synthetic scheme. Since the product here is a secondary alcohol, the scheme could be carried onwards through its oxidation to a ketone and/or its conversion to an alkyl bromide, etc. Let's apply this to a specific example. Suppose we wished to make this compound: We can compare its structure to the general product of the scheme above and figure out what R and R' are. We then plug the specific identities of R and R' into the scheme to arrive at: To summarize, since alcohols can be made into alkyl halides and can also be made into aldehydes and ketones, they are important starting points for carrying out a Grignard synthesis. As products of Grignard syntheses, they are also useful materials to begin a new cycle. The reactions we have looked at today have been those that affected the C-O bond of an alcohol. In making alkyl halides, we broke that bond and made a new bond between the carbon and a halogen. In oxidation, we added a pi bond to the C-O sigma bond of an alcohol. We'll finish today by reminding ourselves of a couple of reactions of alcohols which use their unshared electron pairs, acting as nucleophiles, to make new bonds to carbonyl carbons. One thing to notice about these mechanisms is that the ushared electron pair is used to make the new bond before the O-H bond is broken. That's generally true unless there is a strong base present, something we'll take up next time. Back to the Course Outline The oxidation of an alcohol to form an aldehyde or ketone is very important in synthesis. In this process, the hydroxy hydrogen of the alcohol is replaced by a leaving group (X in the figure below). Then, a base can abstract the proton bound to the alcohol carbon, which results in elimination of the X leaving group and formation of a new carbon-oxygen double bond. As you can see by looking closely at this general mechanism, tertiary alcohols cannot be oxidized in this way – there is no hydrogen to abstract in the final step! Oxidation using chromic acid A common method for oxidizing secondary alcohols to ketones uses chromic acid (H2CrO4) as the oxidizing agent. Chromic acid, also known as Jones reagent, is prepared by adding chromium trioxide (CrO3) to aqueous sulfuric acid. The Jones oxidation also uses acetone as a co-solvent in the reaction to prevent over-oxidation of the organic product. A mechanism for the chromic acid oxidation of a ketone is shown below. Note that the chromium reagent has lost two bonds to oxygen in this reaction, and thus has been reduced (it must have been reduced – it is the oxidizing agent!). Ketones are not oxidized by chromic acid, so the reaction stops at the ketone stage. In contrast, primary alcohols are oxidized by chromic acid first to aldehydes, then straight on to carboxylic acids. It is actually the hydrate form of the aldehyde that is oxidized: One of the hydroxyl groups of the hydrate attacks chromic acid, and the reaction proceeds essentially as shown for the oxidation of a secondary alcohol. Under some conditions, chromic acid will even oxidize a carbon in the benzylic position to a carboxylic acid (notice that a carbon-carbon bond is broken in this transformation). We saw this reaction using KMnO4 in section 16.3; either chromic acid or KMnO4 is suitable, and they give the same carboxylic acid product. A number of other common oxidizing agents are discussed below. The related chromium(VI) compound pyridinium chlorochromate (PCC) is also useful for oxidizing primary alcohols to aldehydes. Further oxidation of the aldehyde to the carboxylic acid stage does not occur, because the reaction is carried out in anhydrous (water-free) organic solvents such as dichloromethane, and therefore the hydrate form of the aldehyde is not able to form. Pyridinium chlorochromate is generated by combining chromium trioxide, hydrochloric acid, and pyridine. The PCC oxidation conditions can both also be used to oxidize secondary alcohols to ketones. Swern oxidation The Swern oxidation uses dimethylsulfoxide and oxalyl chloride, followed by addition of a base such as triethylamine. The actual oxidizing species in this reaction is the dimethylchlorosulfonium ion, which forms from dimethylsulfoxide and oxalyl chloride. The mechanism is included below, for reference: In the first stage dimethylsulfoxide (DMSO) reacts with oxalyl chloride to give an electrophilic sulfur compound, which collapses to give a chlorosulfonium ion, CO2 and CO. In the second stage the alchohol reacts with the chlorosulfonium ion to give a new sulfonium salt and HCl. In the final stage the base (Et3N) is added to deprotonate the salt, which then collapses to give the desired aldehyde or ketone and dimethyl sulfide. Oxidation using silver(I) Silver ion, Ag(I), is often used to oxidize aldehydes to ketones. Two common reaction conditions are: The set of reagents in the latter reaction conditions are commonly known as 'Tollens' reagent'. Video Reactions >> Name Reactions The Jones Oxidation allows a relatively inexpensive conversion of secondary alcohols to ketones and of most primary alcohols to carboxylic acids. The oxidation of primary allylic and benzylic alcohols gives aldehydes. Jones described for the first time a conveniently and safe procedure for a chromium (VI)-based oxidation, that paved the way for some further developments such as Collins Reaction and pyridinium dichromate, which also enabled the oxidation of primary alcohols to aldehydes. Mechanism of the Jones Oxidation The Jones Reagent is a mixture of chromic trioxide or sodium dichromate in diluted sulfuric acid, which forms chromic acid in situ. The alcohol and chromic acid form a chromate ester that either reacts intramolecularly or intermolecularly in the presence of a base (water) to yield the corresponding carbonyl compound: Aldehydes that can form hydrates in the presence of water are further oxidized to carboxylic acids: Some alcohols such as benzylic and allylic alcohols give aldehydes that do not form hydrates in significant amounts; these can therefore be selectively oxidized with unmodified Jones Reagent to yield aldehydes. Although the reagent is very acidic, the substrate in acetone is essentially titrated with the oxidant solution and only very acid-sensitive groups are incompatible. For example esters, even tert-butyl esters, remain unchanged. The concentration of sulfuric acid can be decreased to minimize side reactions, although the oxidation power increases too. Disproportionations and single electron transfers lead to chromium (V) acid and stable Cr(III) hydroxide. The chromium (V) acid promotes a two-electron oxidation of an alcohol and becomes Cr(III). Any residues of toxic Cr(V) and Cr(VI) compounds can be destroyed by the addition of an excess of 2-propanol once the intended reaction is complete. The formation of Cr(III) is indicated by a color change to green. For the synthesis of aldehydes, the Collins Reaction or use of more modern - although more expensive - chromium (VI) reagents such as PCC and PDC can be an appropriate choice. If toxic chromium compounds must be avoided, there are some greener alternative procedures available. For example, molecular oxygen can be used in the presence of palladium as catalyst: synthesis of aldehydes, synthesis of ketones, synthesis of carboxylic acids. Some newer protocols are available in which a catalytic amount of CrO3 in aqueous solution is used in tandem with a strong stoichiometric oxidant, which is able to reoxidize Cr(IV) but does not interfere with the organic compounds. These are also interesting for the development of greener methods, and examples can be found in the recent literature section. A full review of chromium-based reagents can be found in the book written by Tojo and Fernández (Oxidation of Alcohols to Aldehydes and Ketones, Springer Berlin, 2006, 1-97.). Recent Literature Selective oxidation of allylic alcohols with chromic acid K. E. Harding, L. M. May, K. F. Dick, J. Org. Chem., 1975, 40, 1664-1665. A novel chromium trioxide catalyzed oxidation of primary alcohols to the carboxylic acids M. Zhao, J. Li, Z. Song, R. Desmond, D. M. Tschaen, E. J. J. Grabowski, P. J. Reider, Tetrahedron Lett., 1998, 39, 5323-5326. Selective Oxidation of Benzylic Alcohols and TBDMS Ethers to Carbonyl Compounds with CrO3-H5IO6 S. Zhang, L. Xu, M. L. Trudell, Synthesis, 2005, 1757-1760. Selective Oxidation of Benzylic Alcohols and TBDMS Ethers to Carbonyl Compounds with CrO3-H5IO6 S. Zhang, L. Xu, M. L. Trudell, Synthesis, 2005, 1757-1760. Reactions > Organic Synthesis Search Categories: C=O Bond Formation > Synthesis of aldehydes > Name Reactions Claisen Rearrangement Corey-Kim Oxidation Dess-Martin Oxidation Oppenauer Oxidation Swern Oxidation Recent Literature The use of tert-butyl nitrite as the co-catalyst in a 2-azaadamantane-N-oxyl (AZADO)- and 9-azanoradamantane-N-oxyl (nor-AZADO)-catalyzed efficient aerobic oxidation of primary alcohols in MeCN instead of the previously reported AcOH provides the corresponding aldehydes selectively. The addition of saturated aqueous NaHCO3 after the completion of the reaction suppresses the overoxidation of the product during the workup. M. Shibuya, K. Furukawa, Y. Yamamoto, Synlett, 2017, 28, 1554-1557. Cu/TEMPO catalyst systems show reduced reactivity in aerobic oxidation of aliphatic and secondary alcohols. A catalyst system consisting of (MeObpy)CuOTf and ABNO mediates aerobic oxidation of primary, secondary allylic, benzylic, and aliphatic alcohols with nearly equal efficiency. The catalyst exhibits broad functional group compatibility, and most reactions are complete within 1 h at room temperature using ambient air as oxidant. J. E. Steves, S. S. Stahl, J. Am. Chem. Soc., 2013, 135, 15742-15745. A (bpy)CuI/TEMPO catalyst system enables an efficient and selective aerobic oxidation of a broad range of primary alcohols, including allylic, benzylic, and aliphatic derivatives, to the corresponding aldehydes using readily available reagents, at room temperature with ambient air as the oxidant. The catalyst system is compatible with a wide range of functional groups and shows a high selectivity for 1° alcohols. J. M. Hoover, S. S. Stahl, J. Am. Chem. Soc., 2011, 133, 16901-16910. The combination of Fe(NO3)3·9H2O and 9-azabicyclo[3.3.1]nonan-N-oxyl enables an efficient aerobic oxidation of a broad range of primary and secondary alcohols to the corresponding aldehydes and ketones at room temperature with ambient air as the oxidant. L. Wang, S. Shang, G. Li, L. Ren, Y. Lv, S. Gao, J. Org. Chem., 2016, 81, 2189-2193. An efficient bismuth tribromide catalyzed oxidation of various alcohols with aqueous hydrogen peroxide provides carbonyl compounds in good yields. M.-k. Han, S. Kim, S. T. Kim, J. C. Lee, Synlett, 2015, 26, 2434-2436. Oxidation of primary and secondary alcohols, using catalytic amounts of TEMPO and tetra-n-butylammonium bromide in combination with periodic acid and wet alumina in dichloromethane is compatible with a broad range of functional groups and acid-sensitive protecting groups. The system also enables a chemoselective oxidation of secondary alcohols in the presence of primary alcohols. M. Attoui, J.-M. Vatèle, Synlett, 2014, 25, 2923-2927. Sodium hypochlorite pentahydrate crystals with very low NaOH and NaCl contents oxidize primary and secondary alcohols to the corresponding aldehydes and ketones in the presence of TEMPO/Bu4NHSO4 without pH adjustment. This new oxidation method is also applicable to sterically hindered secondary alcohols. T. Okada, T. Asawa, Y. Sugiyama, M. Kirihara, T. Iwai, Y. Kimura, Synlett, 2014, 25, 596-598. The choline- and peroxydisulfate-based environmentally benign biodegradable oxidizing task-specific ionic liquid (TSIL) choline peroxydisulfate (ChPS) was synthesized and characterized. This reagent enables a selective oxidation of alcohols to aldehydes/ketones in very good yields and short reaction time under solvent-free mild reaction conditions without overoxidation to acid. B. L. Gadilohar, H. S. Kumbhar, G. S. Shankarling, Ind. Eng. Chem. Res., 2014, 53, 19010-19018. Imidazolium salts bearing TEMPO groups generate in situ Cu-NHC-TEMPO complexes with commercially available copper powder. These easily available Cu-NHC-TEMPO complexes are quite efficient catalysts for selective, aerobic oxidation of primary alcohols into aldehydes in excellent yields. X. Liu, Q. Xia, Y. Zhang, C. Chen, W. Chen, J. Org. Chem., 2013, 78, 8531-8536. A convenient method enables the preparation of a silica gel supported TEMPO catalyst. The catalyst prepared from [4-hydroxy-TEMPO + NaCl]/SiO2 was used for an aerobic oxidation of alcohols to carbonyls under mild reaction conditions in the presence of Fe(NO3)3 • 9 H2O. Alcohols were converted to the corresponding carbonyls in good to excellent yields. After a simple filtration, the catalyst can be reused at least six times. N. Tamura, T. Aoyama, T. Takido, M. Kodomari, Synlett, 2012, 23, 1397-1407. 2-Iodoxybenzenesulfonic acid, which can be generated in situ from 2-iodobenzenesulfonic acid sodium salt, is a much more active catalyst than modified IBXs for the oxidation of alcohols with Oxone. Highly efficient and selective methods for the oxidation of alcohols to carbonyl compounds such as aldehydes, carboxylic acids, and ketones were established. M. Uyanik, M. Akakura, K. Ishihara, J. Am. Chem. Soc., 2009, 131, 251-262. Swern oxidation using the volatile oxalyl chloride as an activator requires reaction temperatures below -60 °C. 3,3-Dichloro-1,2-diphenylcyclopropene (DDC) can be used as a new activator at −20 °C. This convenient new protocol offers mild and fast reactions. Furthermore, the activator DDC is easy to handle, and diphenylcyclopropenone can be recovered quantitively. T. Guo, Y. Gao, Z. Li, J. Liu, K. Guo, Synlett, 2019, 30, 329-332. In the presence of dimethyl sulfoxide, the Burgess reagent efficiently and rapidly facilitates the oxidation of a broad range of primary and secondary alcohols to their corresponding aldehydes and ketones in excellent yields and under mild conditions. This oxidation can be combined with Wittig olefinations. 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A highly efficient 2,2,6,6-tetramethylpiperidin-1-yloxy (TEMPO) catalyzed reaction using recyclable 1-chloro-1,2-benziodoxol-3(1H)-one as the terminal oxidant allows the conversion of various alcohols to their corresponding carbonyl compounds in high to excellent yields at room temperature in ethyl acetate, which is an environmentally friendly organic solvent. X.-Q. Li, C. Zhang, Synthesis, 2009, 1163-1169. A nitroxyl-radical-catalyzed oxidation using diisopropyl azodicarboxylate (DIAD) allows the conversion of various primary and secondary alcohols to their corresponding aldehydes and ketones without overoxidation to carboxylic acids. 1,2-Diols are oxidized to hydroxyl ketones or diketones depending on the amount of DIAD used. M. Hayashi, M. Shibuay, Y. Iwabuchi, J. Org. Chem., 2012, 77, 3005-3009. Tetrapropylammonium perruthenate enables oxidations of a wide range of molecules including examples of both double oxidations and selective oxidations. Mechanistic studies and general experimental procedures are reported. In addition several interesting developments in the chemistry of this reagent are outlined: heteroatom oxidation, cleavage reactions and use in sequential reaction processes. S. B. Ley, J. Norman, W. P. Griffith, S. P. Marsden, Synthesis, 1994, 639-666. he mild instability of the Ley-Griffith catalyst (TPAP) creates preparation, storage, and reaction reproducibility issues, due to unpreventable slow decomposition. A set of readily synthesized, bench stable, phosphonium perruthenates (ATP3 and MTP3) mirror the reactivity of TPAP, but avoid storage decomposition issues. P. W. Moore, C. D. G. Read, P. V. Bernhardt, C. M. Williams, Chem. Eur. J., 2018, 24, 4556-4561. The use of DMSO in the presence of H2SO4 enables an efficient metal-free oxidation of benzylic alcohols to aromatic aldehydes in excellent yields. This oxidation proceeds in short reaction time without side products. E. Sheikhi, M. Adib, M. A. Karajabad, S. 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