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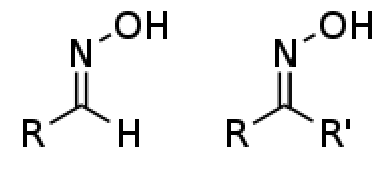
Oxime



An **oxime** is a chemical compound belonging to the imines, with the general formula RR'C=NOH, where R is an organic side-chain and R' may be hydrogen, forming an **aldoxime**, or another organic group, forming a **ketoxime**. O-substituted oximes form a closely related family of compounds. **Amidoximes** are oximes of amides with general structure $R^1C(=NOH)NR^2R^3$.

Oximes are usually generated by the reaction of hydroxylamine with aldehydes or ketones. The term oxime dates back to the 19th century, a combination of the words *oxygen* and *imine*.[1]

Contents

Structure and properties

If the two side-chains on the central carbon are different from each other—either an aldoxime, or a ketoxime with two different "R" groups—the oxime can often have two different geometric stereoisomeric forms according to the *E*/*Z* configuration. An older terminology of *syn* and *anti* was used to identify especially aldoximes according to whether the R group was closer or further from the hydroxyl. Both forms are often stable enough to be separated from each other by standard techniques.

Oximes have three characteristic bands in the infrared spectrum, whose wavelengths corresponding to the stretching vibrations of its three types of bonds: 3600 cm^{-1} (O−H), 1665 cm^{-1} (C=N) and 945 cm^{-1} (N−O).[2]

In aqueous solution, aliphatic oximes are 10^2- to 10^3-fold more resistant to hydrolysis than analogous hydrazones.[3]

Preparation

Oximes can be synthesized by condensation of an aldehyde or a ketone with hydroxylamine. The condensation of aldehydes with hydroxylamine gives aldoximes, and ketoximes are produced from ketones and hydroxylamine. In general, oximes exist as colorless crystals and are poorly soluble in water. Therefore, oximes can be used for the identification of ketone or aldehyde.

Oximes can also be obtained from reaction of nitrites such as isoamyl nitrite with compounds containing an acidic hydrogen atom. Examples are the reaction of ethyl acetoacetate and sodium nitrite in acetic acid,[4][5] the reaction of methyl ethyl ketone with ethyl nitrite in hydrochloric acid.[6] and a similar reaction with propiophenone,[7] the reaction of phenacyl chloride,[8] the reaction of malononitrile with sodium nitrite in acetic acid[9]

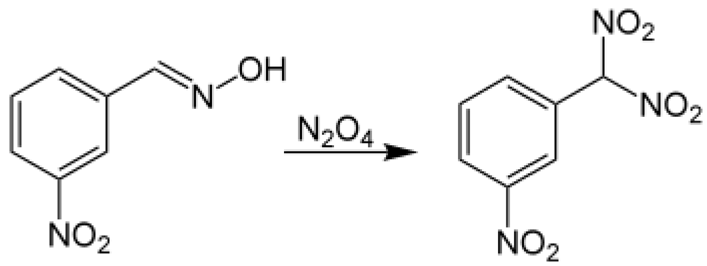
A conceptually related reaction is the Japp–Klingemann reaction.

Reactions

The hydrolysis of oximes proceeds easily by heating in the presence of various inorganic acids, and the oximes decompose into the corresponding ketones or aldehydes, and hydroxylamines. The reduction of oximes by sodium metal,[10] sodium amalgam, hydrogenation, or reaction with hydride reagents produces amines.[11] Typically the reduction of aldoximes gives both primary amines and secondary amines; however, reaction conditions can be altered (such as the addition of potassium hydroxide in a 1/30 molar ratio) to yield solely primary amines.[12]

In general, oximes can be changed to the corresponding amide derivatives by treatment with various acids. This reaction is called Beckmann rearrangement.[13] In this reaction, a hydroxyl group is exchanged with the group that is in the anti position of the hydroxyl group. The amide derivatives that are obtained by Beckmann rearrangement can be transformed into a carboxylic acid by means of hydrolysis (base or acid catalyzed). And an amine by hoffman degradation of the amide in the presence of alkali hypoclorites. Beckmann rearrangement is used for the industrial synthesis of caprolactam (see applications below).

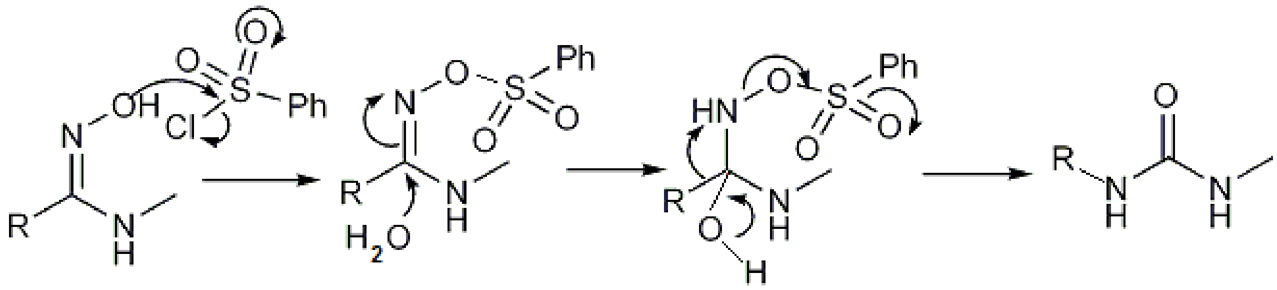
The **Ponzio reaction** (1906)[14] concerning the conversion of *m*-nitrobenzaldoxime to *m*-nitrophenyldinitromethane with dinitrogen tetroxide was the result of research into TNT-like high explosives:[15]



In the Neber rearrangement certain oximes are converted to the corresponding alpha-amino ketones.

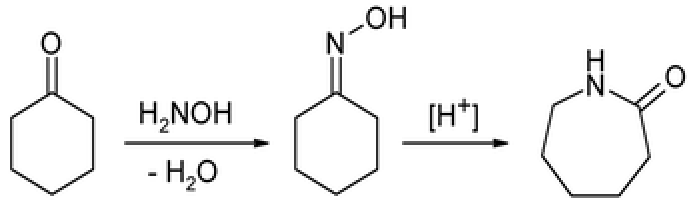
Oximes can be dehydrated using acid anhydrides to yield corresponding nitriles.

Certain amidoximes react with benzenesulfonyl chloride to substituted ureas in the **Tiemann rearrangement**:[16][17]



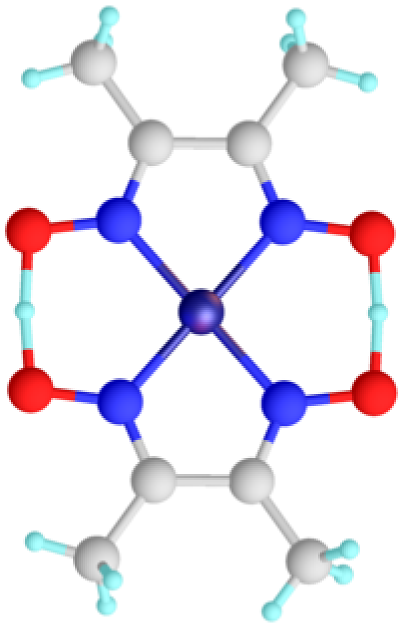
Uses

In their largest application, an oxime is an intermediate in the industrial production of caprolactam, a precursor to Nylon 6. About half of the world's supply of cyclohexanone, more than a million tonnes annually, is converted to the oxime. In the presence of sulfuric acid catalyst, the oxime undergoes the Beckmann rearrangement to give the cyclic amide caprolactam:[18]



Metal extractant

Oximes are commonly used as ligands and sequestering agents for metal ions. Dimethylglyoxime ($dmgH_2$) is a reagent for the analysis of nickel and a popular ligand in its own right. In the typical reaction, a metal reacts with two equivalents of $dmgH_2$ concomitant with ionization of one proton. Salicylaldoxime is a chelator and an extractant in hydrometallurgy.[19]



Structure of Nickel bis(dimethylglyoximate).

Amidoximes such as polyacrylamidoxime can be used to capture trace amounts of uranium from sea water.[20][21] In 2017 researchers announced a configuration that absorbed up to nine times as much uranyl as previous fibers without saturating.[22]

Other applications

- Oxime compounds are used as antidotes for nerve agents. A nerve agent inactivates acetylcholinesterase by phosphorylation. Oxime compounds can reactivate acetylcholinesterase by attaching to phosphorus, forming an oxime-phosphonate, which then splits away from the acetylcholinesterase molecule. Oxime nerve-agent antidotes are pralidoxime (also known as 2-PAM), obidoxime, methoxime, HI-6, Hlo-7, and TMB-4.[23] The effectiveness of the oxime treatment depends on the particular nerve agent used.[24]
- Perillartine, the oxime of perillaldehyde, is used as an artificial sweetener in Japan. It is 2000 times sweeter than sucrose.

- Diaminoglyoxime is a key precursor to various compounds, containing the highly reactive furazan ring.
- Methyl ethyl ketoxime is a skin-preventing additive in many oil-based paints.
- Buccoxime and 5-methyl-3-heptanone oxime ("Stemone") are commercial fragrances.[25]

See also

- Acetone oxime
- Nitrone - the N-oxide of an imine

References

1. The name "oxime" is derived from "oximide" (i.e., oxy- + amide). According to the German organic chemist Victor Meyer (1848–1897) – who, with Alois Janny, synthesized the first oximes – an "oximide" was an organic compound containing the group (=N−OH) attached to a carbon atom. The existence of oximides was questioned at the time (ca. 1882). (See page 1164 of: Victor Meyer und Alois Janny (1882a) "Ueber stickstoffhaltige Acetonderivate" (http://gallica.bnf.fr/ark:/12148/bpt6k90694n/f1165.langEN) (On nitrogenous derivatives of acetone), *Berichte der Deutschen chemischen Gesellschaft*, **15**: 1164–1167.) However, in 1882, Meyer and Janny succeeded in synthesizing methylglyoxime ($CH_3C(=NOH)CH(=NOH)$), which they named "Acetoximsäure" (acetoximic acid) (Meyer & Janny, 1882a, p. 1166). Subsequently, they synthesized 2-propanone, oxime ($(CH_3)_2C=NOH$), which they named "Acetoxim" (acetoxime), in analogy with Acetoximsäure. From Victor Meyer and Alois Janny (1882b) "Ueber die Einwirkung von Hydroxylamin auf Aceton" (http://gallica.bnf.fr/ark:/12148/bpt6k90694n/f1323.image.langEN) (On the effect of hydroxylamine on acetone), *Berichte der Deutschen chemischen Gesellschaft*, **15**: 1324–1326, page 1324: "Die Substanz, welche wir, wegen ihrer nahen Beziehungen zur Acetoximsäure, und da sie keine sauren Eigenschaften besitzt, vorläufig Acetoxim nennen wollen, …" (The substance, which we – on account of its close relations to acetoximic acid, and since it possesses no acid properties – will, for the present, name "acetoxime," …)
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