Beckmann rearrangement reaction pdf

Mechanism of beckmann rearrangement reaction. Beckmann rearrangement reaction example. Beckmann rearrangement regioselectivity. Beckmann mechanism.

Reactions >> Name Reactions An acid-induced rearrangement of oximes to give amides. This reaction is related to the Hofmann and Schmidt Reactions and the Curtius Rearrangement, in that an electropositive nitrogen is formed that initiates an alkyl migration. Mechanism of the Beckmann Rearrangement Oximes generally have a high barrier to inversion, and accordingly this reaction is envisioned to proceed by protonation of the oxime hydroxyl, followed by migration of the alkyl substituent "trans" to nitrogen. The N-O bond is simultaneously cleaved with the expulsion of water, so that formation of a free nitrene is avoided. Recent Literature The Beckmann Rearrangement Executed by Visible-Light-Driven Generation of Vilsmeier-Haack Reagent V. P. Srivastava, A. K. Yadav, L. D. S. Yadav, Synlett, 2014, 25, 665-670. Dichloroimidazolidinedione-Activated Beckmann Rearrangement of Ketoximes for Accessing Amides and Lactams Y. Gao, J. Liu, Z. Li, T. Guo, S. Xu, H. Zhu, F. Wei, S. Chen, H. Gebru, K. Guo, J. Org. Chem., 2018, 83, 2040-2049.
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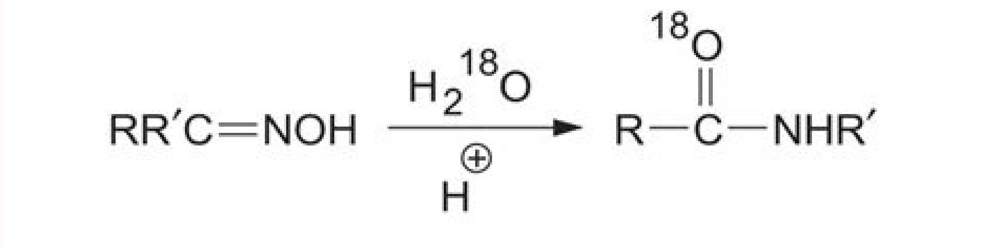

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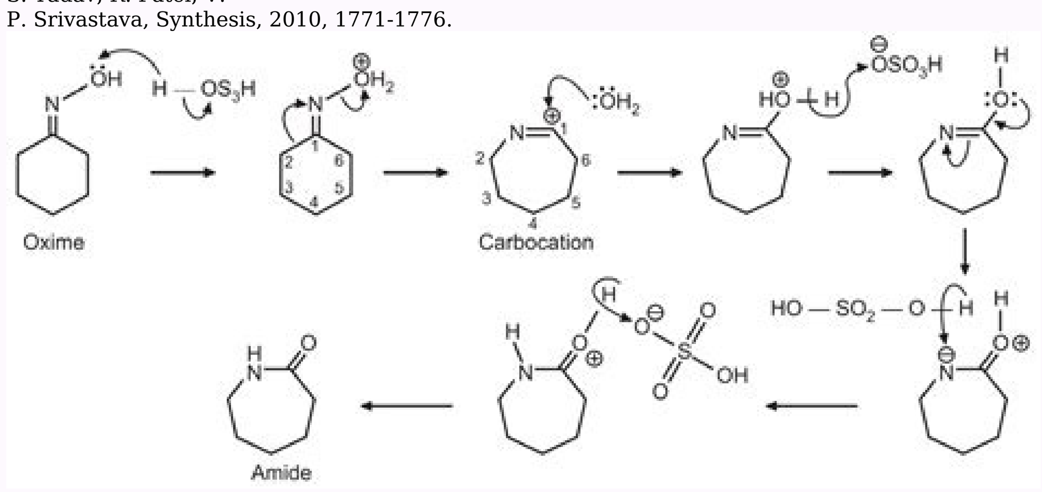
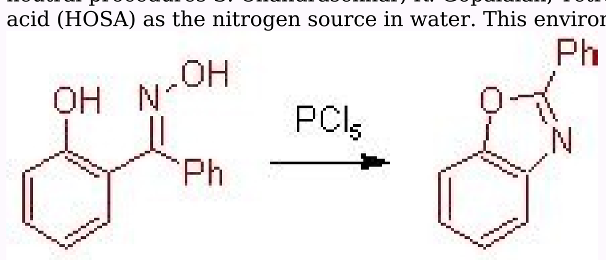


The Reaction of Ketoximes with Hypervalent Iodine Reagents: Beckmann Rearrangement and Hydrolysis to Ketones T. Maegawa, R. Oishi, A. Maekawa, K. Segi, H. Hamamoto, A. Nakamura, Y. Miki, Synthesis, 2022, 54, 4095-4103. Photocatalyzed Triplet Sensitization of Oximes Using Visible Light Provides a Route to Nonclassical Beckmann Rearrangement Products X. Zhang, T. Rovis, J. Am. Chem. Soc., 2021, 143, 21211-21217. Au/Ag-Cocatalyzed Aldoximes to Amides Rearrangement under Solvent- and Acid-Free Conditions R. S. Ramón, J. Bosson, S. Díez-González, N. Marion, S. P. Nolan, J. Org. Chem., 2010, 75, 1197-1202. Beckmann reaction of oximes catalysed by chloral: mild and neutral procedures S. Chandrasekhar, K. Gopalaiah, Tetrahedron Lett., 2003, 44, 755-756. Mercury-Catalyzed Rearrangement of Ketoximes into Amides and Lactams in Acetonitrile C. Ramalingan, Y.-T. Park, J. Org. Chem., 2007, 72, 4536-4538. Zinc(II) catalyzes a single-step protocol for the Beckmann rearrangement using hydroxylamine-O-sulfonic acid (HOSA) as the nitrogen source in water. This environmentally benign and operationally simple method efficiently produces secondary amides under open atmosphere in a pure form after basic aqueous workup. S. Verma, P. Kumar, A. K. Khatana, D. Chandra, A. K. Yadav, B. Tiwari, J. L.



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Solvent-Free and One-Step Beckmann Rearrangement of Ketones and Aldehydes by Zinc Oxide H. Sharghi, M. Hosseini, Synthesis, 2002, 1057-1059. Chemical rearrangement Beckmann rearrangement Named after Ernst Otto Beckmann Reaction type Rearrangement reaction Identifiers Organic Chemistry Portal beckmann-rearrangement RSC ontology ID RXNO:0000026 The Beckmann rearrangement, named after the German chemist Ernst Otto Beckmann (1853–1923), is a rearrangement of an oxime functional group to substituted amides.[1][2] The rearrangement has also been successfully performed on haloimines and nitrones. Cyclic oximes and haloimines yield lactams. The Beckmann rearrangement is often catalyzed by acid; however, other reagents have been known to promote the rearrangement. These include tosyl chloride, thionyl chloride, phosphorus pentachloride, phosphorus pentoxide, triethylamine, sodium hydroxide, trimethylsilyl iodide among others.[3] The Beckmann fragmentation is another reaction that often competes with the rearrangement, though careful selection of promoting reagent and solvent conditions can favor the formation of one over the other, sometimes giving almost exclusively one product. The rearrangement occurs stereospecifically for ketoximes and N-chloro/N-fluoro imines, with the migrating group being anti-periplanar to the leaving group on the nitrogen. Certain conditions have been known to racemize the oxime geometry, leading to the formation of both regioisomers. The rearrangement of aldoximes occurs with stereospecificity in the gas phase and without stereospecificity in the solution phase. A few methodologies allow for the rearrangement of aldoximes to primary amides, but fragmentation commonly competes in these systems. Nitrone rearrangement also occurs without stereospecificity; the regioisomer formed has the amide nitrogen substituted with the group possessing the greatest migratory aptitude. The archetypal Beckmann rearrangement[4] is the conversion of cyclohexanone to caprolactam via the oxime. Caprolactam is the feedstock in the production of Nylon 6.[5] The Beckmann solution consists of acetic acid, hydrochloric acid and acetic anhydride, and was widely used to catalyze the rearrangement. Other acids, such as sulfuric acid, polyphosphoric acid, and hydrogen fluoride have all been used. Sulfuric acid is the most commonly used acid for commercial lactam production due to its formation of an ammonium sulfate by-product when neutralized with ammonia. Ammonium sulfate is a common agricultural fertilizer providing nitrogen and sulfur. Reaction mechanism The most common reaction mechanism of the Beckmann rearrangement consists generally of an alkyl migration anti-periplanar to the expulsion of a leaving group to form a nitrilium ion. This is followed by solvolysis to an imidate and then tautomerization to the amide:[6] This nitrilium ion has been known to be intercepted by other nucleophiles, including the leaving group from the oxime.[3] Presumably after the phenyl group migrates and expels the cyanate, the latter then attacks the nitrilium ion formed. In carbon tetrachloride the isocyanate can be isolated, whereas in ethanol, the urethane is formed after solvolysis of the isocyanate. One computational study has established the mechanism accounting for solvent molecules and substituents.[7] The rearrangement of acetone oxime in the Beckmann solution involved three acetic acid molecules and one proton (present as an oxonium ion). In the transition state leading to the iminium ion (σ-complex), the methyl group migrates to the nitrogen atom in a concerted reaction as the hydroxyl group is expelled. The oxygen atom in the hydroxyl group is stabilized by three acetic acid molecules. In the next step the electrophilic carbon atom in the nitrilium ion is attacked by water and a proton is donated back to acetic acid. In the transition state leading to the imidate, the water oxygen atom is coordinated to 4 other atoms. In the third step, an isomerization step protonates the nitrogen atom leading to the amide. The same computation with a hydroxonium ion and 6 molecules of water has the same result, but when the migrating substituent is a phenyl group, the mechanism favors the formation of an intermediate three-membered π-complex. This π-complex is not found in the H3O+(H2O)6. With the cyclohexanone-oxime, the relief of ring strain results in a third reaction mechanism, leading directly to the protonated caprolactam in a single concerted step without the intermediate formation of a π-complex or σ-complex. Cyanuric chloride assisted Beckmann reaction Beckmann rearrangement can be rendered catalytic using cyanuric chloride and zinc chloride as a co-catalyst. For example, cyclododecanone can be converted to the corresponding lactam, the monomer used in the production of Nylon 12.[8][9] The reaction mechanism for this reaction is based on a catalytic cycle with cyanuric chloride activating the hydroxyl group via a nucleophilic aromatic substitution. The reaction product is dislodged and replaced by new reactant via an intermediate Meisenheimer complex. Beckmann fragmentation The Beckmann fragmentation is a reaction that frequently competes with the Beckmann rearrangement.[3] When the group α to the oxime is capable of stabilizing carbocation formation, the fragmentation becomes a viable reaction pathway. The reaction generates a nitrile and a carbocation, which is quickly intercepted to form a variety of products. The nitrile can also be hydrolyzed under reaction conditions to give carboxylic acids. Different reaction conditions can favor the fragmentation over the rearrangement. Quaternary carbon centers promote fragmentation by stabilizing carbocation formation through hyperconjugation. As shown in the above picture, the "stable" carbocation is formed, which then loses a hydrogen to give a site of unsaturation. Oxygen and nitrogen atoms also promote fragmentation through the formation of ketones and imines respectively. Sulfur is also capable of promoting fragmentation, albeit at a longer range than oxygen or nitrogen. Silicon is capable of directing the fragmentation through the beta-silicon effect. The carbocation intermediate in this reaction is intercepted by nucleophilic fluoride from diethylaminosulfur trifluoride (DAST):[10] Semmler–Wolff reaction The oxime of cyclohexenone with acid forms aniline in a dehydration – aromatization reaction called the Semmler–Wolff reaction or Wolff aromatization [11][12][13][14] The mechanism can be shown as below: The reaction is intrinsically a special case of Beckmann rearrangement combined with neighbouring group participation. Applications in drug synthesis This route also involves the Beckmann rearrangement An industrial synthesis of paracetamol developed by Hoechst–Celanese involves the conversion of a methyl ketone to an acetanilide via a Beckmann rearrangement.[15] The thermal rearrangement that occurs in the synthesis of ketamine was claimed to be a Beckmann rearrangement according to: url. See also Curtius rearrangement Dakin reaction Schmidt reaction Stieglitz rearrangement Lossen rearrangement References ^ Ernst Otto Beckmann (1886). "Zur Kenntniss der Isonitrosoverbindungen" [On [our] knowledge of isonitroso compounds]. Berichte der Deutschen Chemischen Gesellschaft. 19: 988–993. doi:10.1002/cber.188601901222. ^ Donaruma, L. G.; Heldt, W. Z. (1960). "The Beckmann rearrangement. (Review)". Org. React. 11: 1–156. ^ a b c Gawley, R. E. (1988). "The Beckmann reactions: rearrangement, elimination-additions, fragmentations, and rearrangement-cyclizations. (Review)". Org. React. 35: 14–24. ^ Eck, J. C.; Marvel, C. S. (1939). "E-Benzoylaminocaproic Acid". Organic Syntheses. 19: 20. doi:10.15227/orgsyn.019.0020. Archived from the original on 2012-09-28. Retrieved 2005-08-18.
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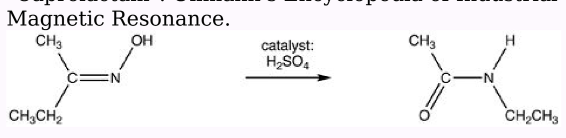

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(Corpus Christi, TX), "Production of acetaminophen", published 13 October 1992, assigned to Hoechst Celanese Corporation (Somerville, NJ) External links Animation of the Beckmann rearrangement Animation of the Beckmann rearrangement (caprolactam) Retrieved from " 2Organic chemical reaction A 1,2-rearrangement or 1,2-migration or 1,2-shift or Whitmore 1,2-shift[1] is an organic reaction where a substituent moves from one atom to another atom in a chemical compound. In a 1,2 shift the movement involves two adjacent atoms but moves over larger distances are possible. In the example below the substituent R moves from carbon atom C2 to C3. The rearrangement is intramolecular and the starting compound and reaction product are structural isomers. The 1,2-rearrangement belongs to a broad class of chemical reactions called rearrangement reactions. A rearrangement involving a hydrogen atom is called a 1,2-hydride shift. If the substituent being rearranged is an alkyl group, it is named according to the alkyl group's anion: i.e. 1,2-methanide shift, 1,2-ethanide shift, etc. Reaction mechanism A 1,2-rearrangement is often initialised by the formation of a reactive intermediate such as: a carbocation by heterolysis in a nucleophilic rearrangement or anionotropic rearrangement a carbanion in an electrophilic rearrangement or cationotropic rearrangement a free radical by homolysis a nitrene. The driving force for the actual migration of a substituent in step two of the rearrangement is the formation of a more stable intermediate.
For instance a tertiary carbocation is more stable than a secondary carbocation and therefore the SN1 reaction of neopentyl bromide with ethanol yields tert-pentyl ethyl ether. Carbocation rearrangements are more common than the carbanion or radical counterparts. This observation can be explained on the basis of Hückel's rule. A cyclic carbocationic transition state is aromatic and stabilized because it holds 2 electrons. In an anionic transition state on the other hand 4 electrons are present thus antiaromatic and destabilized. A radical transition state is neither stabilized or destabilized. The most important carbocation 1,2-shift is the Wagner–Meerwein rearrangement. A carbanionic 1,2-shift is involved in the benzilic acid rearrangement. Radical 1,2-rearrangements The first radical 1,2-rearrangement reported by Heinrich Otto Wieland in 1911[2] was the conversion of bis(triphenylmethyl)peroxide 1 to the tetraphenylethane 2. The reaction proceeds through the triphenylmethoxyl radical A, a rearrangement to diphenylphenoxymethyl C and its dimerization. It is unclear to this day whether in this rearrangement the cyclohexadienyl radical intermediate B is a transition state or a reactive intermediate as it (or any other such species) has thus far eluded detection by ESR spectroscopy.[3] An example of a less common radical 1,2-shift can be found in the gas phase pyrolysis of certain polycyclic aromatic compounds.[4] The energy required in an aryl radical for the 1,2-shift can be high (up to 60 kcal/mol or 250 kJ/mol) but much less than that required for a proton abstraction to an aryne (82 kcal/mol or 340 kJ/mol). In alkene radicals proton abstraction to an alkyne is preferred. 1,2-Rearrangements The following mechanisms involve a 1,2-rearrangement: 1,2-Wittig rearrangement Alpha-ketol rearrangement Beckmann rearrangement Benzilic acid rearrangement Brook rearrangement Criegee rearrangement Curtius rearrangement Dowd–Beckwith ring expansion reaction Favorskii rearrangement Friedel–Crafts reaction Fritsch–Buttenberg–Wiechell rearrangement Halogen dance rearrangement Hofmann rearrangement Lossen rearrangement Pinacol rearrangement Seyferth–Gilbert homologation SN1 reaction (generally) Stevens rearrangement Stieglitz rearrangement Wagner–Meerwein rearrangement Westphalen–Lettré rearrangement Wolff rearrangement References ^ Whitmore, Frank C. (1932). "The common basis of molecular rearrangements". Journal of the American Chemical Society. 54 (8): 3274–3283. doi:10.1021/ja01347a037. ^ Über Triphenylmethyl-peroxyd. Ein Beitrag zur Chemie der freien Radikale Wieland, H.
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