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## Horner wadsworth emmons olefination

General Scheme Reaction Mechanism Page ID23471SAcoros recent examples of Horner-Wadsworth-Emmons reaction in honor of Leopold Horner William S. Wadsworth William D. Emmons Reaction Type Coupling Reaction Chemical Identifiers Organic Portal wittig-horner-reaction RSC onlogy ID RXNO:0000056 The horner-wadsworth-emmons reaction is a chemical reaction used in the organic chemistry of phosphonate carbs stabilized with aldehydes (or keones) to produce predominantly e-alkenes. [1] Base-based desoneration (B-) to generate phosphonate carbanion is shown In 1958, Leopold Horner published a modified Wittig reaction using phosphonate-stabilized carbanions. [3] William S. Wadsworth and William D. Emmons defined the reaction. [5] In contrast to the phosphonium ylides used in wittig's reaction, phosphonate-stabilized carbides are more nucleophilic, but less basic. Similarly, phosphonate-stabilized carbides can be alkylated. Unlike ylides phosphoniums, the byproduct of dialkylphosphate salt is easily removed by aqueous extraction. Several reviews have been published. [11] Reaction mechanism The Horner-Wadsworth-Emmons reaction begins with phosphonate deprotonation to give carbanion phosphonate 1. The nucleophilic addition of carbanion in aldehyde 2 (or ketone) producing 3a or 3b is the rate limiting step. [12] If R2 = H, then intermediates 3a and 4a and intermediates 3b and 4b can intertalk each other. [13] The final elimination of 4a and 4b yield (E)-alkene 5 and (Z)-alkene 6, with the by-product being a dialkyl-phosphate. The ratio of alquenic isomers 5 and 6 depends on the stereochemical result of the initial addition of caranion and the ability of the intermediates to balance. The alpha of the electron withdrawal group (EWG) for phosphonate is necessary for final elimination to occur. In the absence of an electron withdrawal group, the final product is  $\alpha$  hydroxyphosphonate 3a and 3b.[14] However, these  $\alpha$ -hydroxyphosphalates can be transformed into alquenes by reaction with diisopropylcarbodiimide. [15] Stereoselectivity The Horner-Wadsworth-Emmons reaction favors the formation of (E)-alkenes. In general, the greater the balance between the intermediates, the greater the selectivity for (E)-alkene formation. Destitute Alkenes Thompson and Heathcock conducted a systematic study of the 2-methyl acetate reaction (dimethylphosphonous) with several aldehydes. [16] Although each effect was small, they had a cumulative effect making it possible to modify the stereochemical result without modifying the structure of phosphonate. They found higher (E)-esteroselepidia with the following conditions: Increased steric mass of aldehyde Higher reaction temperatures (23 °C over -78 °C) Li &gt; Na &gt; K sais Using the solvent DME on THF In a separate study, he found that bulky phosphonate and bulky groups of electron withdrawal increase the selectivity of E-alkene. Trisubstituted alkenes Most phosphonate and electron withdrawal groups play a critical role in the reaction of branched phosphates  $\alpha$  with aliphatic aldehydes. [17] R1 R2 Alkenratio( E : Z ) Methyl 5 : 95 Methyl Ethyl 10 : 90 Ethyl Ethyl 40 : 60 Isopropil Ethyl 90 : 10 Isopropil Isopropil Isopropil 95 : 5 Aromatic aldehydes produce almost exclusively (E)-alkenes. If aromatic aldehyde (Z)-alkenes are required, the Still-Gennari modification (see below) can be used. Olefination of ketonas The stereoselectivity of the horner-wadsworth-emmons reaction of ketonas is poor to modest. Variations Base-sensitive substrates As many substrates are not stable to sodium hydride, several procedures have been developed using milder bases. Masamune and Roush developed mild conditions using lithium chloride and DBU. [18] Rathke extended this to lithium or magnesium halides with triethylamine. [19] Several other bases were considered effective. [21] [22] Still modification W. Clark Still and C. Gennari developed conditions that give Z-alkenes with excellent stereoselectivity. [23] The use of phosphonates with electron withdrawal groups (trifluoroethyl[24]) along with strongly dissociating conditions (KHMDS and 18-crown-6 in THF) almost exclusive Z-alkene production can be achieved. Ando suggested that the use of electron-deficient phosphonatos accelerates the elimination of oxaphosphian intermediates. [25] See also the reaction of Wittig Michaelis-Arbuzov Reaction Michaelis-Becker Reaction Peterson Reaction Tebbe Olefination References ^ Wadsworth, W. Org. React. 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Organic Syntheses, Coll. Vol. 9, p.88 (1998); Vol. 73, p.152 (1996). (Article) ^ Ando, K. J. Org. Chem. 1997, 62, 1934-1939. (doi:10.1021/jo970057c) Recovered from Horner-wadsworth-emmons (HWE) olefinais is the synthesis of condensation olefins between carbonyl compounds (both aldehydes and ketons) and carbanions derived from phosphine oxides alkyl (Horner's condition), phosphonates (Wadsworth condition and Emmons), phosphonimides (Corey) and their thiono counterparts (Corey). Several advantages of these reactions over wittig's original reaction were discussed. In this reaction, the determining step of the rate is the addition of phosphonate ion in the carbonyl group, where the carbanion-stabilizing group is necessary for elimination to occur; otherwise,  $\beta$ -hydroxyphonaths are formed from unstabilized phosphonates. Several other conditions have been presented that favor selectivity E and selectivity Z. Some mild conditions (LiCl, amine base, room temperature) for the olefination of base-sensitive substrates or phosphonates were introduced. Several other modifications were discussed for this reaction. This reaction was successfully applied to the synthesis of some macrolides and dactylolide. Katerina M. Korch, Donald A. Watson, Cross-Coupling of Heteroatomic Electrophiles, Chemical Reviews, 10.1021/acs.chemrev.8b00628, (2019). The full text of this article iucr.org is unavailable due to technical difficulties. If you are not the author of this article and wish to reproduce material from it in a third-party non-RSC publication, you must formally request permission using the Copyright Clearance Center. Visit our instructions to use the Copyright Release Center page for details. 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If you are the author of this article, you do not need to formally request permission to reproduce figures, diagrams, etc. contained in this article in third-party publications or in a thesis or dissertation, provided that correct recognition is given with the material reproduced. The reproduced material should be assigned as follows: If you are the author of this article, you still need to obtain permission to reproduce the entire article in a third-party publication, with the exception of the reproduction of the entire article in a thesis or dissertation. Information about the reproduction of rsc article material

with different licenses is available on our permission requests page. Page 5 Author affiliations \* Corresponding Authors of the School of Optical-Electrical and Computer Engineering, Shanghai University for Science and Technology, Shanghai 200093, China b Faculty of Science Materials Engineering, China Jiliang Jiliang Hangzhou 310018, China Email: sxucju@163.com Fax: +86-571-28889527 Tel: +86-571-86835781 c School of Mechanical Engineering & Automotive, Zhejiang University of Science and Technology, Hangzhou 310012, China A series of new  $\text{Ce}^{3+}$  activated phosphors and/or  $\text{Sm}^{3+}$  activated  $\text{Y}_4\text{SiAlO}_8\text{N}$  (YSAON) are successfully synthesized by a conventional solid state reaction method. The formation of single-phase YSAON is confirmed by X-ray powder diffraction (XRD) analysis. The crystalline structure of YSAON is resolved by XRD refinement data. DFT calculations indicate that  $\text{Y}_4\text{SiAlO}_8\text{N}$  has an indirect range of 3.819 eV. Based on the analysis of the crystalline structure and life curves, four emission sites of YSAON:0.02Ce<sup>3+</sup>, which are Y1 (413 nm, 448 nm), Y2 (428 nm, 469 nm), Y3 (619 nm, 698 nm) and Y4 (512 nm, 569 nm), respectively are identified. The concentration of Ce<sup>3+</sup> in YSAON is investigated in detail and is confirmed due to dipole-dipole interactions. Spectral measurements of photoluminescence excitation (PLE) and photoluminescence (PL) showed that co-doped phosphor Ce<sup>3+</sup> and Sm<sup>3+</sup> could be efficiently activated by almost UV light, and exhibited four emission bands reached 485 nm, 565 nm, 605 nm and 650 nm, respectively. The CIE chromatic coordinates of the obtained white light can be adjusted by adjusting the contents of Ce<sup>3+</sup> and Sm<sup>3+</sup> ions. Therefore, we anticipate that these materials can be used on white LEDs with almost UV chip. You have access to this article Please wait while we upload your content... Something went wrong. Try again? Back to navigation tab Data of the crystalline structure CIF (6K) New J. Chem., 2016,40, 5458-5466 Download Version (PDF) Y. Hua, X. Li, D. Zhang, H. Ma, D. Deng and S. Xu, New J. Chem., 2016, 40, 5458 If you are not the author of this article and wish to reproduce material from it in a third-party non-RSC publication, you must formally request permission using the Copyright Authorization Center. Visit our instructions to use the Copyright Release Center page for details. Authors who contribute to CSC publications (journal articles, books or book chapters) do not need to formally request permission to reproduce material contained in this article, provided that correct recognition is given with the reproduced material. The reproduced material must be assigned as follows: If the material has been adapted instead of reproduced from the original publication of the Reproduced RSC can be replaced by Adapted. In all cases, Ref. XX is the XXth reference in the reference list. If you are the author of this article, you do not need to formally request permission to reproduce figures, diagrams etc. contained in this article in third-party publications or in a thesis or dissertation, provided that correct recognition is given with material reproduced. The material reproduced should be assigned as follows: If you the author of this article still needs to obtain permission to reproduce the entire article in a third-party publication, with the exception of the reproduction of the entire article in a thesis or dissertation. Information about the reproduction of rsc article material with different licenses is available on our permission requests page. Tweet Share back to tab navigation

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