SYNLETT Spotlight 49

Barium Hydroxide $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$

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This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

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Introduction

Barium hydroxide is a highly valuable reagent, in organic synthesis, due to the availability of the hydroxide ion in solution, the size of the barium counter ion, and for some of its forms, its microcrystalline structure¹ when it is insoluble or partly insoluble in the medium. $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ is the most common form and is commercially available.² Activated barium hydroxide $\text{Ba}(\text{OH})_2$ (C-200),

$[\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}]$ is obtained by heating commercial $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ in an oven at 200 °C for 3 h and powdering the resulting product.³ Barium hydroxide reacts as a base^{4–7} or as a nucleophile,^{8,9} in homogenous^{9,10} or heterogeneous conditions.^{1,4,7,11} Barium hydroxide was revealed to be efficient in deacylations,¹² in Michael addition,³ in aldol or aldol-type condensation,¹³ in Wittig–Horner reactions,^{11,14,15} in Claisen–Schmidt reactions,¹⁶ in Cannizzaro reactions,⁶ and in Suzuki coupling.^{5,10,17}

Abstracts

Reaction of $\text{Ba}(\text{OH})_2$ in absolute EtOH with α -alkyl- α -bromoacetoacetic esters gives the α -bromoester in high yields without saponification or Favorskii rearrangement.⁸ Barium hydroxide proved to be better than sodium ethoxide.⁸

Partially dehydrated $\text{Ba}(\text{OH})_2$ efficiently catalyses the Michael additions of active methylene compounds to chalcones. The yield are significantly better than those obtained in comparative experiments using other basic catalysts.³ A two step mechanism has been postulated: formation of carbanion of acetylacetonate on an active site of the catalyst followed by a surface reaction.¹

Activated $\text{Ba}(\text{OH})_2$ (C-200) has been used as a heterogeneous catalyst in Claisen–Schmidt condensations, which avoid competing Cannizzaro reaction or aldol condensation. Furthermore the reaction time is shorter (1 h vs 30–50 h) than with other alkali metal hydroxides.¹⁶

Horner–Wadsworth–Emmons reaction promoted by $\text{Ba}(\text{OH})_2$ is a mild and efficient method for the coupling of β -ketophosphonates with structurally complex, base-sensitive aldehydes.^{14,18} The barium hydroxide reaction is cleaner and faster to that achieved previously by the Masamune–Roush method (LiCl , Et_3N , MeCN).¹⁹ It promotes efficiently the coupling shown in the scheme where other inorganic bases ($\text{LiOH} \cdot \text{H}_2\text{O}$ for example) failed.¹⁴

Polyether antibiotics appear to complex to barium ions and providing conformations suitable for polydentate ion binding. Lasalocid A has the highest affinity for barium, which has been used to isomerise low affinity epimers to the natural, high affinity aldol.⁷

Opening of the enol-lactone to γ -keto carboxylic acid is readily performed by $\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$ with complete control of the *cis* configuration on the cyclopropane moiety. Use of other hydroxylated bases such as NaOH leads to extensive formation of the *trans*-isomer.⁹

Use of $\text{Ba}(\text{OH})_2$ dramatically improves the yield and accelerates the Suzuki cross-coupling of arenes bearing hindered or electron withdrawing groups.^{5,10,17,20} For example, $\text{Ba}(\text{OH})_2$ produced in a shorter time 4-methylphenylferrocene in 84% yield instead of 25% yield with sodium carbonate.⁵

α -Arylation of diethyl malonate was readily performed in almost quantitative yields by using an homogeneous catalyst and $\text{Ba}(\text{OH})_2 \cdot \text{H}_2\text{O}$ as heterogeneous base.⁴

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