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Spotlight 49

Barium Hydroxide Ba(OH)₂·8H₂O
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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 structure when it is insoluble or partly insoluble in the medium. Ba(OH)₂·8H₂O is the most common form and is commercially available. Activated barium hydroxide Ba(OH)₂ (C-200), [Ba(OH)₂·H₂O] is obtained by heating commercial Ba(OH)₂·8H₂O in an oven at 200 °C for 3 h and powdering the resulting product. Barium hydroxide reacts as a base or as a nucleophile, in homogenous or heterogeneous conditions. Barium hydroxide was revealed to be efficient in deacylations, in Michael addition, in aldol or aldol-type condensation, in Wittig–Horner reactions, in Claisen–Schmidt reactions, in Canizzaro reactions, and in Suzuki coupling.

Abstracts

Reaction of Ba(OH)₂ in absolute EtOH with α-alkyl-α-bromoacetoacetic esters gives the α-bromoester in high yields without saponification or Favorskii rearrangement. Barium hydroxide proved to be better than sodium ethoxide.

Partially dehydrated Ba(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. A two step mechanism has been postulated: formation of carbanion of acetylacetone on an active site of the catalyst followed by a surface reaction.

Activated Ba(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.

Horner–Wadsworth–Emmons reaction promoted by Ba(OH)₂ is a mild and efficient method for the coupling of β-ketophosphonates with structurally complex, base-sensitive aldehydes. The barium hydroxide reaction is cleaner and faster to that achieved previously by the Masamune–Roush method (LiCl, Et₃N, MeCN). It promotes efficiently the coupling shown in the scheme where other inorganic bases (LiOH·H₂O for example) failed.
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. Openning of the enol-lactone to γ-keto carboxylic acid is readily performed by Ba(OH)$_2$·H$_2$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.

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

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

References

(2) (a) Catalogue number Sigma-Aldrich, 21,757-3 (b) Catalogue number Acros, 42346-5000
(14) Paterson, I.; Yeung, K.-S.; Smaill, J. B. *Synlett* 1993, 774.