

Debromination of *endo*-(+)-3-Bromocamphor with Primary Amines

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A desbromação redutiva da *endo*-(+)-3-bromocânfora com diferentes aminas primárias seguida da formação de imina foi investigada. Esta reação requer procedimento experimental simples sem qualquer solvente orgânico, metal ou agente de redução convencional. Observou-se uma forte influência da polaridade da amina na eficiência do processo de desbromação, e que etanolamina e etilenodiamina tendo pontos de ebulições elevados o suficiente podem desbromar 3-bromocânfora fornecendo canfoniminas em bons rendimentos. Os mecanismos de desbromação da 3-bromocânfora com etanolamina e *n*-hexilamina foram investigados no nível B3LYP/6-311+G(d,p). Revelou-se o mecanismo radical, e que a reação com etanolamina mais polar é energeticamente mais favorável.

Reductive debromination of *endo*-(+)-3-bromocamphor with different primary amines followed by imine formation was investigated. This reaction requires simple experimental procedure without any organic solvent, metal or conventional reducing agent. A strong influence of amine polarity on the efficacy of debromination process was observed, and ethanolamine and ethylene diamine having sufficiently high boiling points can debrominate 3-bromocamphor giving corresponding camphanimines in good isolated yields. The mechanisms of debromination of 3-bromocamphor with ethanolamine and *n*-hexylamine were investigated at the B3LYP/6-311+G(d,p) level of theory. The radical mechanism was revealed, and it was shown that the reaction with more polar ethanolamine is energetically more favorable.

Keywords: 3-bromocamphor, primary amines, reductive debromination, reaction mechanism, DFT

Introduction

The debromination of α -bromoketones plays an important role in the synthetic organic chemistry as one of the most useful reaction for the construction of more complex organic molecules. A number of reagents have been reported for the debromination of α -bromocarbonyl compounds such as triphenylphosphine,¹ pyridinium salts,² molybdenum hexacarbonyl,³ sodium iodide-chlorotrimethylsilane,⁴ triphenylphosphonium iodide,⁵ sodium borohydride-antimony tribromide,⁶ sodium

amalgam,⁷ tributyltin hydride,⁸ zinc in acetic acid,⁹ aqueous titanium trichloride,¹⁰ tellurium reagents,¹¹ nickel boride,¹² selenium,¹³ sodium dithionite,¹⁴ inorganic phosphorus compounds¹⁵ and ionic liquids.¹⁶

On the other hand, a central need of different synthetic transformations in the last years, especially in pharmaceutical industry, is the preparation of compounds that are derived from the chiral sources. Among these compounds, *vic*-amino alcohols obtained from D-camphor¹⁷ and ketimines prepared from camphor-imine¹⁸ serve as template for many applications in asymmetric synthesis. Camphor-based imino alcohols are precursors for preparation of chiral aryl phosphates in the role of

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