

Tuning the anionic cyclization-protonation of *N*-benzyl(diphenyl)-phosphinamides. Highly efficient synthesis of tetrahydrobenzo-1-aza-2 λ^5 -phospholes containing a 1,3-cyclohexadiene system

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Dedicated to Prof. J. Elguero and Prof. P. Molina on the occasion of their 70th and 65th birthdays, respectively

Abstract

A study of the dearomatization of *N*-alkyl-*N*-benzyl(diphenyl)phosphinamides through anionic cyclization followed by protonation with a wide range of protonating reagents has been carried out. The proton sources used include alcohols, phenols, amines, amides, and organic acids. The effect of the *N*-alkyl substituent, the acidity, and the size of the protonating reagent were analyzed. The mixtures of products formed were derived predominantly from α - and γ -protonation with respect to the phosphorus. Addition of *tert*-butyldimethylsilyl chloride to the reaction medium prior to the protonation with methanol allowed the preparation of tetrahydrobenzo-[c]-1-aza-2 λ^5 -phospholes containing a 1,3-cyclohexadiene with a *cis*-fusion of the rings in very high yields.

Keywords: Phosphinamides, dearomatization, anionic cyclization, [1,3]-cyclohexadienes, protonation, azaphospholes

Introduction

Dearomatizing reactions through anionic cyclization and subsequent electrophilic quenching represent an attractive approach to the preparation of functionalized alicyclic compounds, and have received great attention in the last five years.¹

Anionic cyclization onto an unactivated aromatic ring generally leads to aromatized products, owing to the harsh reaction conditions used and/or the absence of electron-withdrawing