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Theoretical study of the Wittig, aza-Wittig and arsa-Wittig reactions of $\text{Me}_3\text{P}=\text{XH}$ ylide ($\text{X}=\text{CH}, \text{N}$ and As) with cyclic ketones in the gas phase and solution phase

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Abstract: A computational study of the comparative reactivity of the Wittig, aza-Wittig and arsa-Wittig reactions of cyclopentanone and cyclobutanone with $\text{Me}_3\text{P}=\text{XH}$ ylide ($\text{X}=\text{CH}, \text{N}$ and As) in the gas phase has been performed at B3LYP/6-31G** level of theory. Calculations have also been performed using integral equation formalism polarizable continuum model (IEFPCM), with THF solvent at B3LYP/6-31G** level of theory. In the gas phase as well as in solvent, these reactions were predicted to be two step processes with two complexes R and P (reactant complex and product complex), two transition states, one for addition (TS1) and the other for elimination (TS2) and two four-membered cyclic intermediates (INT1 and INT2), except that INT2 was not found in the aza-Wittig reaction. In our calculations, the Wittig reaction is found to be more favorable both thermodynamically and kinetically than aza- and arsa-Wittig reactions. The Wittig reaction is found to be more exothermic and to involve a lower activation barrier to formation of INT1 than the aza and arsa-Wittig reactions. The activation barriers in the reactions of cyclopentanone are higher as compared to the reaction of cyclobutanone in gas phase and solution phase. The addition activation barriers for each reaction are overestimated in the solvent model as compared to gas phase reactions.

Keywords: Wittig reaction – aza-Wittig reaction – arsa-Wittig reaction – cyclic ketone – cyclopentanone – cyclobutanone

1. Introduction

In 1919, iminophosphoranes isoelectronic with methylenephosphoranes (Wittig reagent), were first synthesized by Staudinger and Meyer [1]. These have drawn much attention both experimentally and theoretically because of their wide application in organic synthesis. The aza-Wittig reaction [2-3] in which iminophosphoranes can react with carbonyls, is one of the best methods to form a $-\text{C}=\text{N}-$ double bond (imine group). Imines ($\text{R}_2\text{C}=\text{NR}'$), one of the products from the aza-Wittig reaction are important intermediate compounds in organic synthesis due to their versatile chemical and physical properties and are also used in coordination chemistry [4-5].

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