

## Effect of Anchimeric Assistance in Addition Reaction of Bifunctional Tertiary Phosphines to Electron-Deficient Alkenes

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### Abstract

© 2016 Wiley Periodicals, Inc. Bifunctional tertiary phosphines with hydrogen-bonding functionalities have recently received a considerable amount of attention due to their efficient application in organocatalysis. To estimate the potential role of the carboxyl group in specific interactions with reaction intermediates, the kinetics of the reactions of 2-(diphenylphosphino)benzoic acid (2-DPPBA) and 4-(diphenylphosphino)benzoic acid (4-DPPBA) with acrylic acid and acrylonitrile was studied in different solvents, and the data were compared with the results obtained previously for the related reactions of triphenylphosphine. The solvent effect on the reaction kinetics was found to be identical to all of the phosphines, suggesting that H bonding with the solvent has no specific influence on the rate for bifunctional tertiary phosphines. Despite of the electron-withdrawing effect of the carboxyl group, the rate of reaction of 2-DPPBA with acrylic acid is 1.4-2.1 times larger than that of triphenylphosphine, implying participation of the neighboring CO<sub>2</sub>H group of the phosphine in stabilization of the intermediate zwitterion by intramolecular H bonding with the carbonyl oxygen atom of the acrylic acid as a proton acceptor center. The results show that this trend of reactivity was not applicable when acrylonitrile was used as an electrophilic partner since the 2-DPPBA was less reactive than triphenylphosphine. The presence of sp-hybridized atoms of the nitrile group makes intramolecular H bonding with the nitrogen atom of the generated zwitterion strongly disfavored, but leaves the possibility for the H bonding with  $\pi$  electrons of the CN group. Similar effects of anchimeric assistance were not observed for the 4-DPPBA due to disability of the carboxyl group in the para position to participate in any intramolecular H bonding with the reaction intermediates.

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