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Regioselective Phosphorylation of Ambident Anions and Electrophilic Reaction of Carbanion of Allyl-Phosphonate

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REGIOSELECTIVE PHOSPHORYLATION OF AMBIDENT ANIONS AND ELECTROPHILIC REACTION OF CARBANION OF ALLYL-PHOSPHONATE

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A study on the regioselectivity of phosphorylation reaction of ambident anions of phenylacetone and Schiff base derived from cyclohexylamine and acetophenone or acetone was reported. The behaviour of allylbenzene in phosphorylation reaction was also examined. The phosphorylation of dianions of phenylacetone gave two C-phosphorylation products together with a O-phosphorylated compounds consisting of Z and E isomers. Upon phosphorylation of ambident anions of Schiff base from cyclohexylamine and acetophenone or acetone three parallel reactions occurred with C-phosphorylation predominating. In the presence of excess phosphorylation agent N,N-bisphosphorylated was also formed.

For the evaluation of the structural effects governing the regioselectivity of electrophilic reaction, the structure of the carbanion of allylphosphonate in a series of solvent was studied by ^1H , ^{13}C and ^{31}P NMR at low temperature. In reaction with n-butyllithium in an aprotic solvent at -50°C , both localized and delocalized allyl anions were found. As shown by ab initio calculation the total energy of these isomers are very similar while the negative charge of the α -carbon are significantly higher than that of the γ -carbon. Meanwhile, the energy of the HOMO are varied depending on the structure and conformation of the anions.