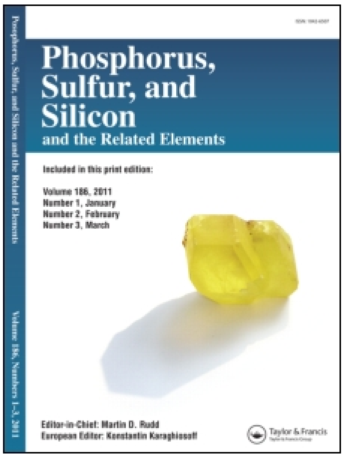

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Gancarz, Roman , Gancarz, Irena and Masiowska, Agnieszka(1996) 'Nucleophilic Addition to Carbonyl Compounds. Competition Between Hard (Amine) and Soft (Phosphite) Nucleophile', Phosphorus, Sulfur, and Silicon and the Related Elements, 111: 1, 195

To link to this Article: DOI: 10.1080/10426509608054824

URL: http://dx.doi.org/10.1080/10426509608054824

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 195
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NUCLEOPHILIC ADDITION TO CARBONYL COMPOUNDS. COMPETITION BETWEEN HARD (AMINE) AND SOFT (PHOSPHITE) NUCLEOPHILE

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In the reaction mixture of carbonyl compound, amine and diethyl phosphite several different reactions are observed. The formation of aminophosphonate (Kabachnik- Fields reaction) is frequently accompanied with the formation of hydroxyphosphonate (Pudovik reaction) or product of its rearrangement.[1-3] This is due to the presence of one electrophile (carbonyl compound) and two nucleophiles (amine and phosphite) in the reaction mixture, which may compete for the electrophilic center.

We have studied the reaction for various carbonyl compounds by means of the ^{1}H and ^{31}P NMR and also by performing the kinetic experiments. We have measured the formation of imine in the reaction of carbonyl compound with excess of butylamine and also the formation of hydroxyphosphonate in the reaction of carbonyl compound with diethyl phosphite in the presence of tertiary amine.

Analyzing the data obtained from kinetic experiments and NMR studies we have observed that the preference of hydroxyphosphonate path over the imine path becomes stronger once we move from aliphatic to aromatic aldehydes or ketones.

We have found that this can be neither due to the changes of electrophilicity of the carbonyl center nor to the steric factors. The only parameter consistent with the observations is the Pearson's hardness and softness parameters.[4]

Thus the competition between two reactions can be explained as the interaction of soft phosphorus nucleophile with soft aromatic carbonyl compound and hard nitrogen nucleophile with hard aliphatic carbonyl compound. Aliphatic carbonyl compounds form predominantly imines and aminophosphonates. The change toward formation of hydroxyphosphonates are observed after replacing the aliphatic substituent into aromatic one. Hydroxyphosphonates are formed predominantly for bisaromatic ketones. We have found a good correlation between our data and the softness parameters calculated by GRINDOL[5] program.

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