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Highly Selective Arbuzov Reaction of α -Chlorocarbonyl Compounds with $P(OEt)_3$ and Substituted Amino Urea

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HIGHLY SELECTIVE ARBUZOV REACTION OF α-CHLOROCARBONYL COMPOUNDS WITH P(OEt)₃ AND SUBSTITUTED AMINO UREA

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Abstract A facile one—pot Arbuzov reaction of α-chlorocarbonyl compounds with P(OEt)₃ and substituted amino urea is described. The highly selective Arbuzov reaction of α-chlorocarbonyl compounds could take place under relatively mild conditions, giving products in high yields.

Key Words Arbuzov reaction, a-Chlorocarbonyl compound, P(OEt), Selective reaction

As it has been known, Arbuzov reaction of RX can be easily carried out. Whereas the reaction of a-chlorocarbonyl compounds with P(OR), usually takes an alternative course of Perkow reaction. Herein, we report a facile one—pot method in which the Arbuzov reaction of a-chloroacetone and trichloroacetaldehyde could selectively be carried out and provide products in relatively high yields (see scheme I).

Scheme 1

Both the compounds 2 and B, and products 3 and C are important blocks for building complex molecules. The compounds 2 and B are all new compounds, and confirmed by ¹H NMR, IR, and Elemental Analysis.

The ¹¹P NMR data of 2 and B showed that there were two isomers ($\delta = 23.42$ and 24. 90ppm, when R=H in the compound 2), which probably resulted from cis and trans isomers of the imine double bonds.

By the determination of ³¹P NMR, it has been found that the rate of above Arbuzov reaction is directly proportional to both reaction temperature and solvent polarity. An acidic catalyst is also necessary to accelerate the above reaction.

In addition, the order adding the starting materials into reaction system is another key factor for raising reaction selectivity. Only after a-chlorocarbonyl compound reacted with substituted amino urea for 1—2hr, could P(OEt), be added dropwise, especially when the a-chlorocarbonyl compound is trichloroacetaldehyde.

[1] Shokol V. A. and Kozhushko B. N., Russ Chem. Rev., 54 (1), 98(1985).