Stereoselective Synthesis of Trisubstituted Olefins

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A new method for the highly stereoselective synthesis of trisubstituted olefins is presented. The method involves the stereoselective construction of various β-hydroxy phosphonamidates followed by their thermolysis to provide trisubstituted olefins in extremely high geometrical purity (>99/1).

The stereoselective construction of β-hydroxy phosphonamidates could be accomplished through three main synthetic transformations. The first involves the acylation of various parent 1,3,2-oxazaphospholidines to provide monoalkylated β-keto phosphonamidates in good yield. The second step is the alkylation of the β-keto phosphonamidates to provide α,α-dialkylated β-keto phosphonamidates in high yield and very high diastereoselectivities. Finally, the highly diastereoselective reduction of the dialkylated β-keto phosphonamidates could be accomplished through the use of a variety of reducing agents to give β-hydroxy phosphonamidates in high yield and high diastereoselectivities.

Thermolysis of the diastereomerically pure β-hydroxy phosphonamidates gave a variety of trisubstituted olefins in high yield and very high stereoselectivity. A discussion on anionic mediated olefinations as well as an extension into the stereoselective synthesis of tetrasubstituted olefins is also presented.

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PHOSPHORYLATED BROMONITROETHENES IN THE REACTIONS WITH NH- AND CH- ACIDS

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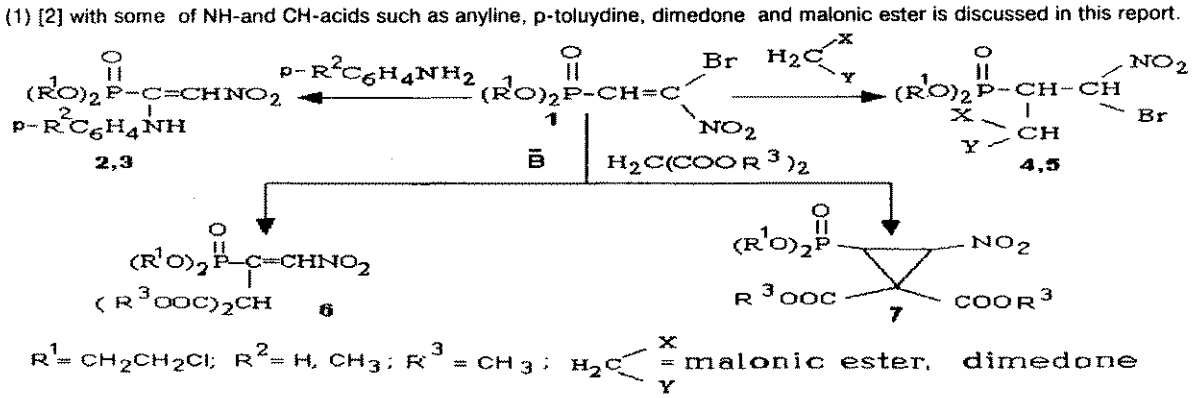
The highly reactive halonitroethenes attract the attention of scientists so as they are active synthons in the synthesis of various classes of organic compounds. [1]. Phosphorylated halonitroethenes can represent particular interest, because of phosphoryl group introduction "a priori" makes the reactivity of such compounds to be higher and allows to synthesize the wide number of biologically active compounds. The very first study of interaction between O,O-di(2-chloroethyl)-2-bromo-2-nitroethenephosphonate (1) [2] with some of NH-and CH-acids such as anyline, p-toluydine, dimedone and malonic ester is discussed in this report.



$R^1 = CH_2CH_2Cl$; $R^2 = H, CH_3$; $R^3 = CH_3$; $H_2C\langle^{X}_{Y}$ = malonic ester, dimedone

Reactions with aromatic amines were found to proceed according to addition - elimination mechanism and result in recently unknown phosphorylated nitroenamines (2,3). Reactions with dimedone and malonic ester result in addition products (4, 5) or proceed further to form products of dehydrohalogenation. For example, the reaction with malonic ester under the catalysis of sodium methylate excess results in the synthesis of substituted nitroethenephosphonate (6) and nitrocyclopropanephosphonate (7). The structure of synthesized compounds is proved by methods of mass-spectrometry, IR, UV and ^{1}H, ^{13}C, ^{31}P NMR spectroscopy.

[1] Perekalin V.V., Lipina E.S., Berestovitskaya V.M., Efremov D.A. Nitroalkenes. Wiley and Sons, England. 1994. C. 169-182.
[2] Botata J.E, Deyko L.I., Kostina T.K., Baranov G.M., Berestovitskaya V.M. // Zh. Obshch. Khim. 1994.: in printing.