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REACTIONS OF α-FORMYL-α-CHLORCYCLONONES AND γ-BUTYROLACTONE WITH S-TRIMETHYLSILYL ESTER OF DIALKYLDITHIOPHOSPHORIC ACID

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Abstract α -Formyl- α -chlorsubstituted cyclonones or α -formyl- α -chlor- γ -butyrolactone react with O,O-diizopropyltrimethylsilyldithiophosphate to give adducts which rearrange thermaly to α - dithiophosphoryl contained β -dicarbonic compounds.

In our previous studies we have shown that silyl esters of semithioacetals of α -chlor- β -oxo and α -phosphoryl- α , α -dichlorosubstituted aldegydes rearrange to 1,3- and 1,2-dicarbonic compounds or α -ketophosphonates contained chlorthioesters, respectively. The main reason for our current interest is the reactions of α -formyl- α -chlorcyclonones (Ia, b) and α -formyl- α -chlor- γ -butyrolactone (Ic) with dialcoxy-S-trimethylsilyldithiophosphates (II). Stable adducts (IIIa, c) are formed by reactions of oxoaldegydes (Ia, c) with dithiophosphates (II).

la-c II IIIa-c

The spectral date (IIIa, c) are consistent with the mixture stereomers (1H NMR: two dublets (CH) J=15Hz). Upon heating, (IIIa, c) rearrange to α -dithiophosphoryl substituted 1,3-dicarbonic compounds (Va, c) followed by elimination of trimethylchlorsilan and migration of phosphoryl group. We suggest the formation of oxiranes (IVa, c) in this reaction.

Va-c Va-c

The interaction of chlorcontained hydroxydithiophosphate (VIa, c) obtained from the reaction of (Ia, c) and dithiophosphoric acids, with natrium hydrid affords isomeric adducts (Va, c), instead of oxiranes (IVa, c).

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