

# Orthoamide und Iminiumsalse, LXXXVI [1]. Ein weiterer Beitrag zur Chemie der Trialkoxyacetonitrile

Orthoamides and Iminium Salts LXXXVI [1].

A Further Contribution to the Chemistry of Trialkoxyacetonitriles

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An improved procedure for the preparation of trimethoxyacetonitrile (**3a**) starting from trichloroacetonitrile and sodium methanolate is described. Carbanions, obtained by the action of sodium hydride on nitriles, ethyl acetate and methylketones, react with trialkoxyacetonitriles **3** to give  $\alpha$ -imino-orthocarboxylic acid trialkylesters **12**, **14** and **20**, which form an equilibrium with the tautomeric enamines **13**, **15** and **21**. The enamines **21** react with *N,N*-dimethylformamide dimethylacetal (**24**) to give amidines **25** which are cyclized to pyridinium salts **28** and **29** on treatment with benzyl bromide and acetyl chloride, respectively. The reaction of the enamionitrile **13a** with the orthoamide derivative of phenylpropionic acid **30** affords the pyridine-2-orthocarboxylic acid trimethylester **31**.

The *N, O*-protected 4-hydroxy-piperidine **35** can be deprotonated by means of *sec*-butyl lithium. The carbanions thus formed are trapped with D<sub>2</sub>O, dimethyl sulfate, phenylisocyanate, CO<sub>2</sub>, and dimethyl carbonate delivering the piperidine derivatives **37–41**. The heterocyclic orthoester **43** can be prepared analogously from **35** and **3a**. The piperidine derivatives **44**, **46** and **47** are prepared from the *N, O*-protected piperidines **39** and **41**.

*Key words:* Trialkoxyacetonitriles, Carbanions, Addition,  $\alpha$ -Imino Carboxylic Acid Orthoesters, Pyridinium Salts, Pyridines, 4-Hydroxypiperidine Derivatives