Ref: Contract No. DAJA 45-85-C-0016 ("New Synthetic Approaches to TAT")

FIRST INTERIM REPORT (ITEM 0001)

This is a short note to inform you that the research work on the project named above has been started on July 1, 1985. The months before, intense literature searches have been carried out, using also Chemical Abstracts on-line recherches.

Mr. Dipl.-Chem. Johannes Nagelschmitz is named as the first researcher in this project. After completing some additional literature searches he will concentrate on chemical approaches to methyleneimines possessing suitable stabilizing groups, like silylimines.

Preparation of these compounds is planned using a method developed by C. Krüger, E.G. Rochow and U. Wannagat, Chem. Ber. 96, 2132 (1963):

\[
\begin{align*}
\text{H}_2\text{N} &+ \text{Na}^+ \text{In} (\text{SiMe}_3)_2 \rightarrow \text{H}_2\text{N} - \text{SiMe}_3^+ \\
&+ \text{NaOSiMe}_3
\end{align*}
\]

These silylimines can be easily acylated:

\[
\begin{align*}
\text{H}_2\text{N} - \text{SiMe}_3 & \xrightarrow{\text{AcO}} \text{O} \text{SiMe}_3 + \text{H}-\text{Ac}^+
\end{align*}
\]

(cf. R. Kupfer, S. Meier and E.U. Würchwein, Synthesis 1984, 688). In case that these compounds prove to be instable, these reactive imines should be produced in the presence of complexing transition metals.
Another approach to be investigated in this first phase is gas phase thermolysis of 5-methyl-5(4H)-oxazolone (i.e. an azlactone or anhydride of N-acetyl-glycine):

Other examples for this thermolysis are known (cf. S. Jendrzejewski and W. Steglich, Chem.Ber. 114, 1337 (1981)). The resulting acetyl-ethyleneimine should be at once intercepted by complexation to a transition metal.

Furthermore, retrodienic reaction of azabicyclo[2.2.1]hept-5-enes can be useful for obtaining acylimines:

Thermolysis of hexahydro-2-triazines and hexamethylenetetramine are to follow.

The second researcher for this project will be most probably Mr. Dipl.-Chem. Marcus Bongen. Although, the discussion of his definite theme is not yet finished, Mr. Bongen will be going to try another approach to methyleneimines in the aqueous system, via the historical pathway of E.A. Werner, J.Chem. Soc. 1917, 844 starting from ammoniumchloride and formaldehyde involving methyleneimine-hydrochloride (cf. our "Appendix", sent 1.8.1983, p. 5), which is expected to be intercepted and directed to a cyclotetramerization reaction with a complexing metal:

Furthermore, variation of the classical urotropine synthesis carried out under typical template conditions in the presence of a transition metal will belong to the actual research program of Mr. Bongen, which will be described in more detail in my second interim report.

(Prof. Dr. H. Wamhoff)
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