In pursuing new synthetic approaches to TAT, the project has been further developed in the meantime on several promising new pathways.

1) Report on the work of Dipl.-Chem. Marcus Bonnen

Among the other current reactions studied by Mr. Bonnen (see previous Interim Reports), we are trying now additionally electrochemical degradation reactions of the urotropine (hexamethylenetetramine) molecule. The following picture shows a typical cyclic voltammetry of the urotropine:

As the picture demonstrates, first orientation experiments in this field employing a platinum cathode and a glassy carbon anode reveal clearly, that urotropine is attacked by electrooxidation. Thereby, the 1st oxidation potential is a sharp and distinctive peak, which points to a definite chemical transformation...
The 2nd oxidative potential, however, is much more broad and therefore unspecific. The chemical degradation observed during this electrooxidation process can be formulated as an oxidative transformation of a -CH₂-N-moiety, first into -CH=N- and subsequent oxidative removal of the CH₂- bridging unit, e.g.:

\[
\begin{align*}
\text{N} & \quad \text{N} \\
/ & \\
\text{N} - \text{CH₂} & \rightarrow \text{N} - \text{CH} = \text{N} \\
/ & \\
\text{N} & \\
\end{align*}
\]

As a consequence, this electrooxidation might originate a selective removal of methylene bridges in urotropine, leading finally to monocyclic TAT-systems. This assumption depicted in the primary rather optimistic analytical investigations prompt us to try preparative electrochemical experiments of urotropine in a divided cell equipped with a glassy carbon anode and a pt-wire cathode. Thus, in a typical procedure, MeOH is used as solvent, at ambient temperature, LiClO₄ as conducting salt, urotropine is added in a 0.2 M concentration. The constant current is 100 mA with a voltage of 14-18 V, so that the current density is about 110 mA/cm². The whole process is monitored by TLC, and as the first experiment has shown, besides some unchanged urotropine, just one new and pure product can be detected by TLC. Separation and elucidation of the structure are currently investigated.

**Carbonyl Analogs of TAT**

If urotropine is decomposed at high temperatures by acetylchloride N,N-Bis(chloromethylene)-acetamide is obtained (cf. Liebigs Ann.Chem. 1979, 1450):

\[
\begin{align*}
\text{MeCOCl} & \quad \Delta \\
\text{Me-CO-N} & \quad \text{N} \\
/ & \\
\text{N} & \\
\end{align*}
\]

In an independent approach involving in a 2:2-manner this latter product a combination was undertaken with t.-but-amine in the following manner:

\[
\begin{align*}
\text{Ac-N} & \quad \text{N} \\
/ & \\
\text{N} & \\
\end{align*}
\]

But instead of the expected product, a mixture of several unidentifiable substances has been furnished. But more experiments of this type will be carried out in the future employing also the Template effect with several Metal ions.
Furthermore, dimethylurea has been condensed with phosgene to get the following carboxylic acid chloride (or ester, depending on work-up):

\[
\begin{align*}
\text{O=NNHMe} & \quad \text{+ COCl}_2 & \rightarrow & \quad \text{O=NNHMe} & \quad \text{EtOH} & \rightarrow & \quad \text{O=NNHMe} \\
& & & & & & \text{O=NNMe} \\
\end{align*}
\]

In a further step this carbamoyl chloride is tried to react with a second dimethylurea, and then ring closure is attempted with another equivalent of phosgene:

This work is under progress.


Among other leads depicted in former interim reports, Mr. Nagelschmitz tries in his experimental work to develop preparative methods for silylated methyleneimines as building units of TAT:

\[
4\text{N-SiMe}_3 \quad \text{BuLi} \rightarrow \quad \text{LiN-SiMe}_3 \quad \text{HCHO} \rightarrow \quad \text{H}_2\text{C=N-SiMe}_3
\]

The final product is expected to tetramerize upon treatment with complexing transition metal ions.

Mr. Nagelschmitz also succeeded in the resynthesis of the known t.-but-methyleneimine (according O.S.-procedure from t.-but.-amine and aq 37% HCHO):

\[
\text{t.-but-N}_2 \quad + \quad \text{HCHO} \rightarrow \quad \text{H}_2\text{C=N-t-but}
\]

Thus, he has got now the first time a stable methyleneimine in hands for proving its tetramerization tendency in the presence of Me\(^{2+}\), as follows:

\[
\text{H}_2\text{C=N-t-but} \quad + \quad \text{Me}^{2+} \quad \rightarrow \quad \text{N-t-but} \quad + \quad \text{Me}^{2+}
\]

Very helpful in this connection might be a recent publication of a Roumanian group, which we have detected incidentally by literature search: M. Brezeanu,
and D.-N. Marinescu-Stefanescu, Analele Universitatii Bucuresti Chimii 1973, 22(1), 21 (Chem.Abstr. 81, 98800 f (1974)), where 1,3,5,7-Tetraphenyl-1,3,5,7-tetraazacyclooctane ("TTO") has been obtained besides hexaazacyclododecane and dodekaazacyclotetraicosane systems by template effect of metal ions (Co$^{2+}$) on HCHO solved in DMF and aniline in the ratio: 1 Co$^{2+}$ : 6 aniline : 6 formaldehyde. The intermediate is Ph-N=CH$_2$. We try to repeat first this reaction, which can be performed entirely in aqueous solution and which is significantly influenced by Template catalysis.

Then we are planning to transform this tetramerization to other suitable methyleneimines, like the formentioned t.-but-methyleneimine and Me$_3$Si-methyleneimine.

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