Dear Dr. Squire,

in the following I am sending you a

BRIEF REPORT

ON A VISIT, CONFERENCE, AND DISCUSSIONS WITH DR. EVERETT E. GILBERT
US-ARMY ARMAMENT, MUNITIONS AND CHEMICAL COMMAND, PICATINNY AREAL,
DOVER/NJ ON JULY 21, 1986

Arrival time (by rental car) at Picatinny Areal: 9:30 a.m.
Departure time: 2:00 p.m.

Dr. Everett E. Gilbert received me at the Visitors Entrance of Picatinny Areal and we went in his car to the Chemistry Laboratory.

After arrival we had an intense, stimulating and fruitful conference where I reported to Dr. Gilbert and one of his colleagues on our recent results in novel TAT syntheses. The overhead folios shown during my seminar are attached to this report.

As a result, new promising ways for the synthesis of TAT have been discussed in detail, and on the base of an exchange of results obtained meanwhile both in our laboratories in Bonn and in the laboratories of Dr. Gilbert Dover/NJ, numerous new experiments are to follow, which will be described also in the FOURTH INTERIM REPORT.
(ITEM 0004), which follows within the next weeks.

Especially, more interest should be cast on DAPT,

\[ \text{Ac-}N\backslash\text{N}\backslash\text{N}-\text{Ac} \]

which can be easily obtained by a procedure of E.E. Gilbert et al. Propellants & Explosives 6, 67 (1981) and references cited therein; all methods of destructing the internal methylene bridge should be studied in detail on this target molecule.

Furthermore, a reaction of urea with formaldehyde is strongly suggested which should afford a carbonyl-bridged urotropine, such as:

\[ \text{N} \]

Special interest should also be paid to a well known tetramethylene-disulfotetramine described by Hecht and Henecka, Angew.Chem. 61, 365 (1949).

With the aid of trivalent phosphorus compounds (deoxygenation) or by photochemical extrusion reaction (selective excitation) transformations of this highly bioactive compound could be studied in detail, but all work on this compound must be carried out very cautiously, due to its high convulsive activity.

With best regards,

(Prof. Dr. H. Wamhoff)

enclosures: folio copies
Strategies for TAT Synthesis

A) UROTOPINE ROUTE

(a) Partial Destruction of Urotopine

- Thermal decomposition
- Destruction with reactive agents
- Electrooxidation

(b) Controlled Approach by Classical Urotopine Synthesis

\[ \text{CH}_2O + \text{NH}_3 \rightarrow [\text{CH}_2 = \text{NH}_2] \text{Me}^{2+} \rightarrow \text{TAT} \]

(c) Oxo-TAT Approaches

Strategies for TAT Synthesis

B) METHYLENEIMINE ROUTE

(d) Generation of Methyleneimines

- In free state (only with suitable substitute)
- In situ generation and interception

\[ \text{H}_2\text{C} = \text{N} - \text{R} \xrightarrow{\text{Me}^{2+}} \text{R}^- \text{N} \text{Me}^{2+} \text{Cl} \text{Cl}]_2 \text{Cl} = \text{N} - \text{R} \rightarrow \text{TAT} \]

*) Suitable: stabilizing, easy removable
Urotropine Degradation

\[
\text{"} X_2 \text{"} \rightarrow \text{CH}_2 X_2 + \text{TMS} \rightarrow \text{N} \text{--N--TMS} \\
\text{Me}_3 \text{SiCl}
\]

\[
" X_2 " = \text{POCl}_3 \\
\text{PPH}_3 / \text{C}_2 \text{H}_6 \rightarrow \text{Cl}_2 \text{PPH}_3 \\
\text{PPH}_3 / \text{CCl}_4 \rightarrow \text{PH}_3 \text{P}^{+} \cdots \text{Cl} \cdots \text{CCl}_3 \\
\text{PXs} \text{; no selective degradation} \\
\text{Br}_2 \text{PPH}_3 \text{; U. remains stable} \\
\text{or total destruction} \\
( \rightarrow \text{N} \text{H}_4 \text{X} ) \\
\text{Reflexing with TMS} \rightarrow \text{(also autoclave)} : \therefore \\
\text{N-Chlorosuccinimide} / \text{CCl}_4 \text{; at RT} \rightarrow \therefore \\
\text{A reflux; total destruct} \\
\text{planned: MeCN / NCS -10°C} \rightarrow \text{RT} \text{; longer period}
\]

Electrooxidative Degradation of Urotropine

First orientating experiments

Undivided cell: \text{MeOH} - \text{NacIO}_4 - 4 \text{U} : \text{no effect} \\
\text{MeOH} - \text{NacIO}_4 - 10 \text{U} : \text{degradation} \\
\Rightarrow \text{inorganic prod}

Critical Voltage Range: 5 - 10 U

Galvano STATIC experiment: current constant, 2 electrode Voltage Varying

Now under investigation: \text{(in Metrohm cells)}

Potentiostatic experiment: current constant Voltage constant against reference electrode

MeCN / ~ 5 U \Rightarrow \text{Urotropine recovered + substrate}

MeCN / \text{Ac}_2 \text{O} / ~ 5 U \text{ in progress}
Carbonyl Analogs of TAT

\[
\text{NHMe} + \text{CO}_2 \rightarrow \text{N-} + \text{CO}_2
g_{\text{NHMe}} + \text{E} \rightarrow \text{N-} + \text{E} + \text{CO}_2
\]

Reduction of Ureas:

\[
\text{NH}_2 \xrightarrow{\text{LiAlH}_4} \text{H}_2\text{C} \xrightarrow{\text{LiAlH}_4} \text{H}_2\text{C} \xrightarrow{\text{further reactions}} \text{NHR}_2
\]

Planned experiment:

\[
\text{NH} + \text{but} \xrightarrow{\text{LiAlH}_4} \text{H}_2\text{C} \xrightarrow{\text{further reactions}} \text{NHR}_2
\]


Hofmann Degradation

Experiment currently under investigation
Routes to Methylene imines

Steglich route:

\[
\begin{align*}
\text{H}_2\text{C} = \text{O} & \quad \text{gives} \quad \text{MeCN} \\
\text{H}_2\text{N-} -\text{Me} & \quad \text{gives} \quad \text{Pyrolysis} \\
\text{H}_2\text{C} = \text{N-} -\text{Me} & \quad \text{no working-up} \quad \text{and purification possible}
\end{align*}
\]

Breuer route:

\[
\text{H}_2\text{C}=\text{O} + \text{H}_2\text{N-} -\text{Me} \rightarrow \text{H}_2\text{C}<\text{N-} -\text{Me} \quad \text{Ez} \quad \text{H}_2\text{C}=\text{N-} -\text{Me}
\]

Wannagat – Württemburg Route:

\[
\text{H}_2\text{C}=\text{O} + \text{Na}^+ [\text{N-(SiMe}^3\text{)}_2] \rightarrow \text{H}_2\text{C}=\text{N-SiMe}^3 + \text{NaO(SiMe}^3\text{)}
\]

Stable + But - Methylenamine

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

Tetramerization tendency now investigated:

\[
\begin{align*}
\text{H}_2\text{C}=\text{N-} + \text{but} & \quad \text{Me}^{2+} \\
\text{H}_2\text{C}=\text{N-} + \text{but} & \quad \text{CO}_2
\end{align*}
\]

With \( \text{Zn}^{2+}, \text{Cd}^{2+} \) no result

now running: \( \text{Co}^{2+}, \text{Cu}^{2+}, \text{Ni}^{2+} \)
END
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