AD-A194 590 BRIEF REPORT ON A VISIT CONFERENCE AND DISCUSSIONS WITH 1/1
DR EVERETT E GILB (U) BONN UNIV (GERMANY F R)
H WAMHOFF 29 JUL 86 DAJA45-85-C-0016

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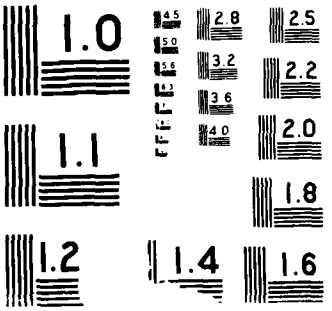
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INSTITUT FÜR ORGANISCHE CHEMIE
UND BIOCHEMIE
DER UNIVERSITÄT BONN

Prof. Dr. H. Wamhoff

Gerhard-Domagk-Straße 1
D - 5300 Bonn 1, 29.7.1986
☎ (0228) 731
Bei Durchwahl 732651, 732671
Telex 886657 unibo d

Dr. David R. Squire PhD, Director
European Research Office
USARDSG(UK) - Chemistry Branch
Edison House
223 Old Marylebone Road
GB - London NW1 5TH ENGLAND

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

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.

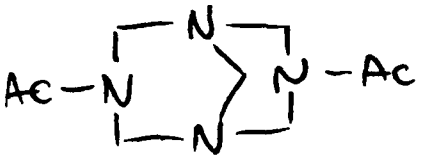
Dr. Everett E. Gilbert received me at the Visitors Entrance of Picatinny Areal and we went in his car to the Chemistry Laboratory.

After arrival we had an intense, stimulating and fruitful conferenc 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,



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:

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) UROTROPINE ROUTE

(a) Partial Destruction of Urotropine

→ thermal decomposition

"X_2" → destruction with reactive agents

e^- → electrooxidation

(b) Controlled Approach by Classical Urotropine Synthesis

$$CH_2O + NH_3 \longrightarrow [CH_2=NH_2] \xrightarrow{Me^{2+}} TAT$$

(c) Oxo-TAT Approaches

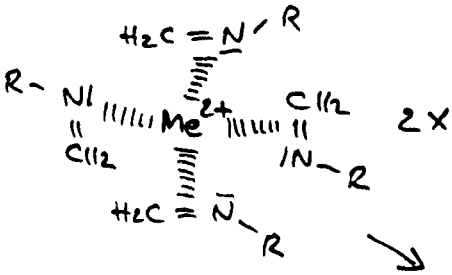
Strategies for TAT Synthesis
B) METHYLENEIMINE ROUTE

(d) Generation of Methyleneimines

⇒ in free state (only with suitable*) substitue

⇒ in situ generation and interception

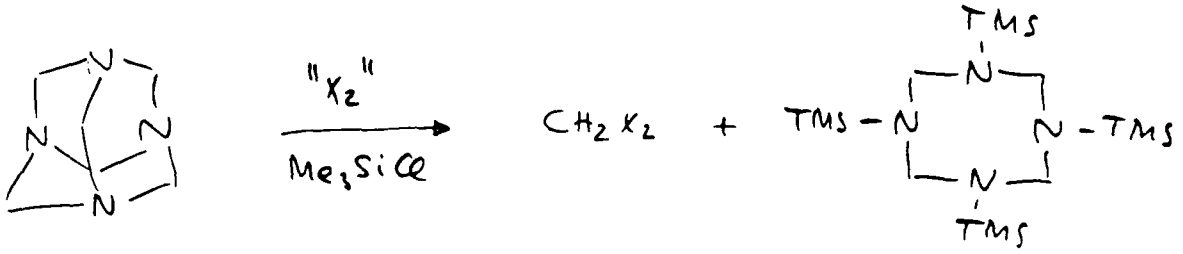
$$H_2C=N-R \xrightarrow{Me^{2+}}$$



→ TAT

*) suitable: stabilizing
easy removable

Urotropine Degradation



"X_2" = $POCl_3$

$PPh_3 / C_2Cl_6 \Rightarrow Cl_2PPh_3$

$PPh_3 / CCl_4 \Rightarrow Ph_3P^+ \cdots Cl \cdots \bar{C}Cl_3$

PX_5 no selective degradation

Br_2PPh_3 U. remains stable
... or total destructio
($\Rightarrow NH_4X$)

Refluxing with TMSCl (also autoclav) : ÷

N-Chlorosuccinimide / CCl_4 at RT° : ÷
Δ reflux : total destruct

planned: MeCN / NCS $-10° \rightarrow$ RT° Longer perio

Electrooxidative Degradation of Urotropine

First orientating experiments

Undivided cell : MeOH – $NaClO_4$ – 1 U : no effect
MeOH – $NaClO_4$ – 10 U : degradation
⇒ inorganic prod

Critical voltage range : 5 – 10 U

galvanostatic experiment: current constant, 2 electrode
voltage varying

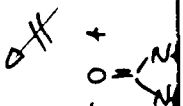
now under investigation: (in Metrohm cells)

potentiostatic experiment: current constant
voltage constant
against reference electrode

MeCN / ~ 5U ⇒ Urotropine recovered + substanz

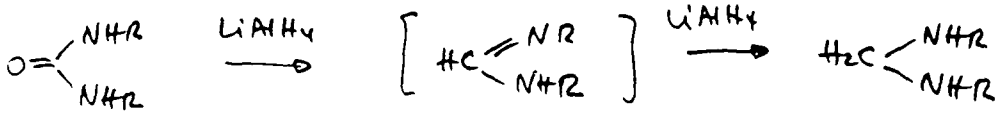
MeCN / Ac_2O / ~ 5U in progress

Carbonyl Analogs of TAT



no further reaction

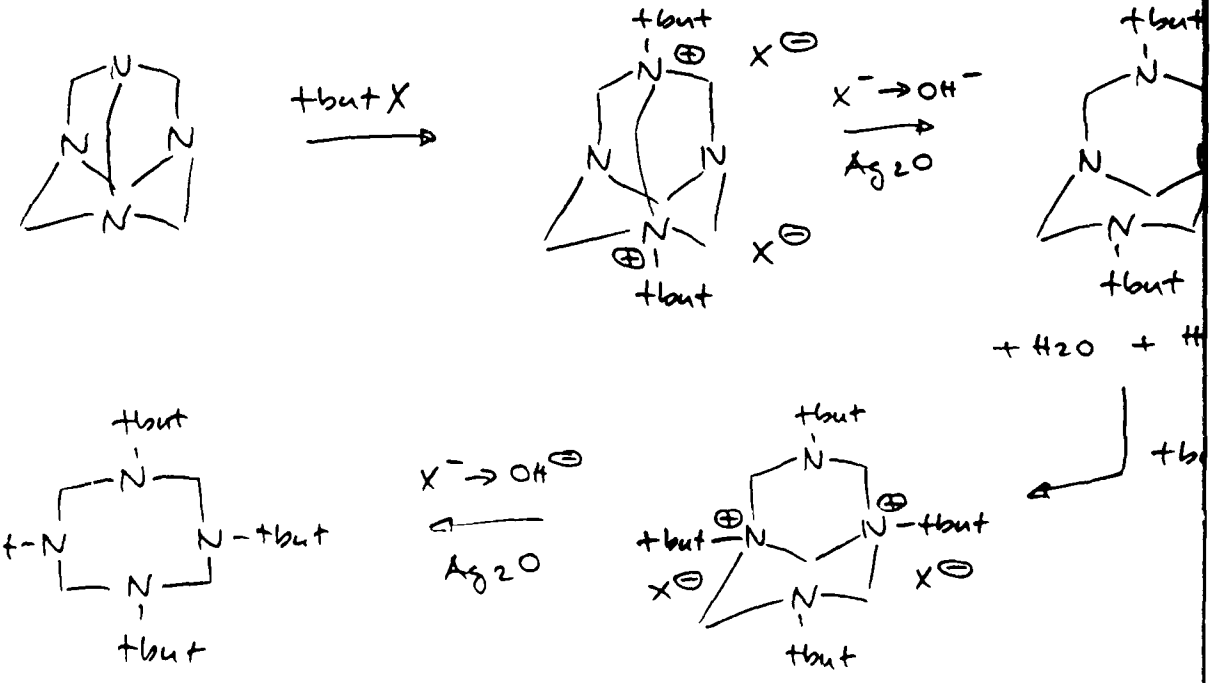
Reduction of Ureas:



planned experiment:

Lit.: G. Lettieri, A. Larizza, G. Brancaccio, P. Monforte, Atti Soc. Peloritana Sci. Fis. Mat. Nat. 24 (1) 77 (1978); C.A. 92, 94028 (1978)

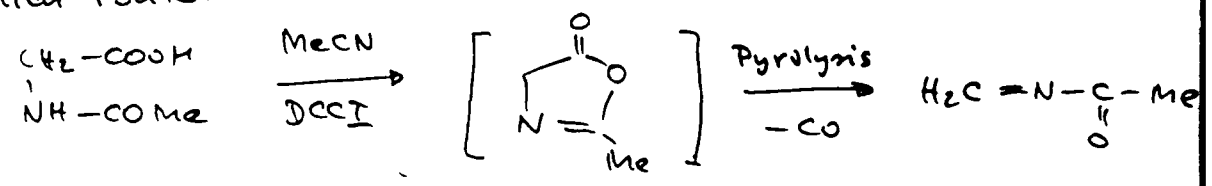
Hofmann Degradation



experiment currently under investigation

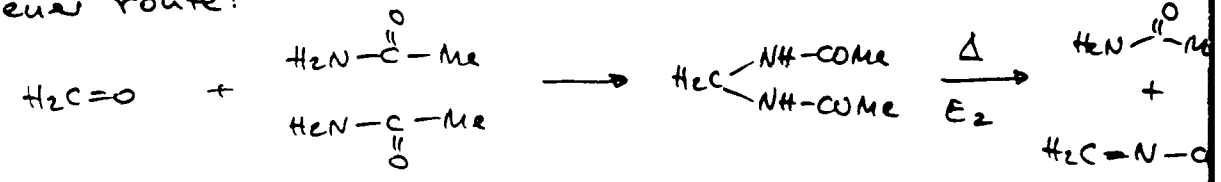
Routes to Methyleneimines

Steglich route:

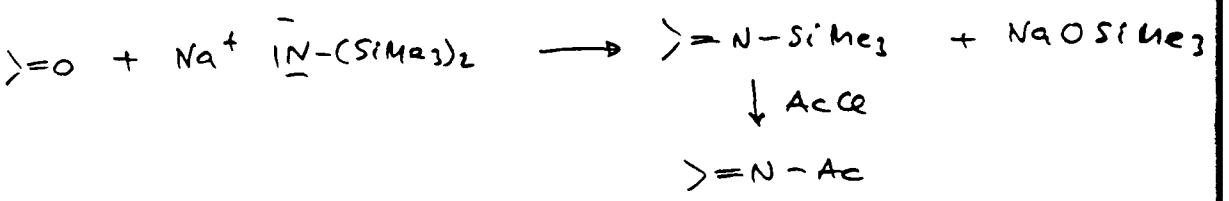


no working-up nl. purification possib

Breuer route:

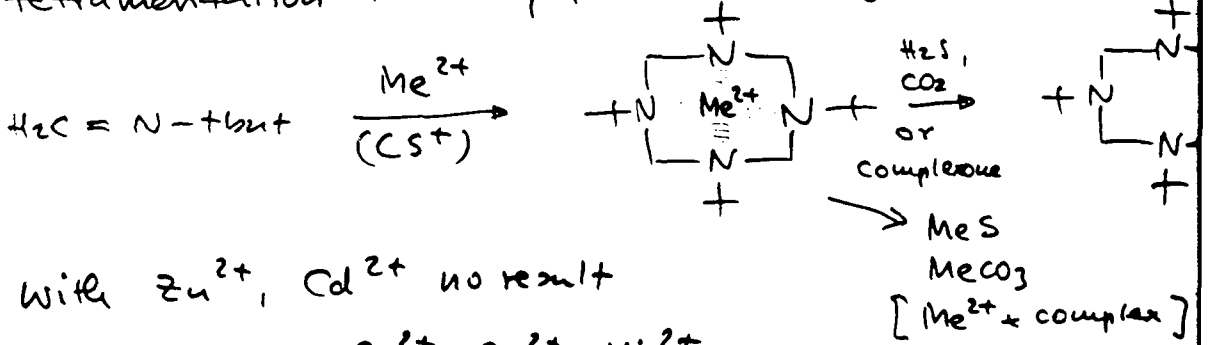


Wannagat - Würthwein route:



Stable +But - methyleneimine

tetramerization tendency, now investigated:



With Zn^{2+}, Cd^{2+} no result

now running: Co^{2+}, Cu^{2+}, Ni^{2+}

END
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