SYNTHESIS OF HIGH-ENERGY 1,2,3,4-TETRAZINE 1,3-DI-N-OXIDES AND PENTAZINE POLY-N-OXIDES

At the Contemporary Energetics Conference at The MITRE Corporation, McLean, VA on July 20, 2003. In this talk I summarized our DARPA/AFOSR and published Russian efforts to prepare DTTO, IsoDTTO and other energetics. In the present set of overheads I have added further routes (overheads 35, 43, 46 and 50-59) to be investigated for synthesis of various 1,2,3,4-tetrazine, 1,3-di-N-oxides, DTTO, and IsoDTTO. Synthesis of triazolotetrazine dioxides (overhead 35) is now being emphasized. There are notes and explanations on almost all of the overheads to make them more understandable. Such additions were suggested at our June meeting, 2004. I believe that the additions make our work and my talk much more intelligible. In the present overheads our studies of synthesis of 1-nitroacetylenes and dinitroacetylene as sponsored by DARPA/AFOSR have not been included.
Synthesis of 1,2,3,4-Tetrazines, 1,2,3,4-Tetrazine Di-N-oxides, Pentazole Derivatives, Pentazine Poly-N-oxides, and Nitroacetylenes

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This presentation will be primarily a review of research on the chemistry of 1,2,3,4-tetrazines and 1,2,3,4-tetrazine di-N-oxides as published from Moscow since 1988 by many chemists in the Ioffe Institute and as explored by Dr. Venugopal at OSU since early 2001. In this talk, many new and interesting structures will be considered and, if time permits, many approaches to synthesis of energetic molecules will be proposed.
Stabilized Systems
Alternate Positive-Negative Charges (APNC)

This is truly an important concept in considering new syntheses of high-energy materials!

This concept should be made clear to every student of beginning chemistry.

The concept of APNC was originated by Menkin, a theoretician in Russia, and serves as the basis for my presentation today. The ideas will be extended to many new energetic molecules as yet unknown.

Menkin, 1988; Churakov, 1991

X = O, NR, and CR₂

Substitute N for O in nitrate (NO₃⁻), nitrite (NO₂⁻), pernitrate (O₃NO₃⁻) and related oxygen-nitrogen compounds (N-O₇, RONO, RO₃, etc.)
Stabilized N-Oxides

unstable

Many chemists in the 1940s tried to prepare N₆, a benzene analog.

This molecule has not been isolated very easily at low temperatures. Is it unstable? Can it be isolated?

This molecule undergoes loss of nitrogen to give benzene.

unstable

This tetraazine N-oxide loses N₂ to form o-dinitrobenzene.

No one has examined this molecule at low temperatures.

stable, usable

This molecule is stable, new readily prepared, and melts at 172-174°C.

very few chemists know that this molecule, N₂O, will go through a mass spectrometer. This molecule is a trimmer of nitrous oxide, N₂O.

The Zelinski chemists have been studying this molecule since the early 1990s or even earlier. They have been studying this molecule.

This tetraazine N-oxide melts at 72-74°C and can be kept for 6-7 hours before decomposition.

Prof. Bartlett visited OSU and was informed of the APNC concept. He and his colleagues have calculated that 2 is more stable than 1 and 5 is more stable than 3 and 4. As yet 2 has not been prepared.
Synthesis of High-Energy Heterocycles

We at OSU are studying preparation, stability, and utility of 1,2,3,4-tetrazines at low temperatures. If such tetrazines can be utilized, this whole area must become very important and economical.

DTTO: An extremely important molecule. Synthesis of DTTO is the major objective of the DG-3 BARPA-Air Force research efforts. This molecule is truly important, the Russians are keeping their studies secret!!!

SN2TTO: an extremely important molecule also being studied in Russia. A major objective of the program by DG-3 BARPA/AIR FORCE at OSU. See calculations in a later slide.

A very important molecule whose synthesis is being studied at OSU. This molecule should be an excellent source of N2O for use in rocket engine and combustion chambers. DARR project.

We are beginning study of synthesis of this molecule at OSU. New engines and combustion machines.

Calculations are in progress.
The research of Dr. Venugopal at OSU is totally dedicated to practical synthesis of DTTO or/and IsoDTTO. This project needs additional funding if Dr. Venugopal is to stay at OSU and complete this effort.

DTTO
(The better molecule)

IsoDTTO

This slide illustrates the APNE characters of DTTO and IsoDTTO. The alternating positive and negative charges in the ring systems are illustrated.

Talbovski emphasized the concept in his West Coast seminar in 1995. We should learn where the Russians and the Chinese are in syntheses of DTTO and IsoDTTO. Are these molecules going to be practical?
Compound 1 has been synthesized in Moscow and at CAS. It is hoped to convert 1 to 2 or 3, as yet this effort has not been successful. Compounds 2 and 3 are isomers of DTTO and SSDTO.

At present we do not have good crystals of 1. We want an X-ray analysis of 1 (tetrazine 1,3-di-N-oxide). Identifying the structures of the hydrolysis products of 1 will take time. Study has been initiated of study of synthesis of 4. This study needs further funding.
Alternating Positive-Negative Heterocycles

These molecules have been theorized by Hückel to be stable! These molecules lead to proposals of study of polymerization and copolymerization of \( N_2O \) and azides \( (2N_3) \). Chemists should really study fixation of \( N_2O \) and \( 2N_3 \)! Later slides will amplify such studies!
$$\rho = 2.419 \text{ g cm}^{-3}$$
$$\Delta H_f = 179.5 \text{ kcal mol}^{-1}$$
$$P_{CJ} = 131.4 \text{ GPa}$$

$$\rho = 2.484 \text{ g cm}^{-3}$$
$$\Delta H_f = 175.7 \text{ kcal mol}^{-1}$$
$$P_{CJ} = 131.8 \text{ GPa}$$

Do such a monocyclic compounds stable or practical?

$$\rho = 2.072 \text{ g cm}^{-3}$$
$$\Delta H_f = 134.3 \text{ kcal mol}^{-1}$$
$$P_{CJ} = 50.6 \text{ GPa}$$

Will these molecules be this dense?

$$\rho = 2.191 \text{ g cm}^{-3}$$
$$\Delta H_f = 128.6 \text{ kcal mol}^{-1}$$
$$P_{CJ} = 61.8 \text{ GPa}$$

These calculations were made by H. Ammon at the University of Maryland. DTTO and ISO- DTTO are spectacular!
Compounds 1, 2, and 3 have been synthesized in Moscow. They are quite stable. We are sure that preparation of 5 is being attempted by Belinsky chemists.
Carbon Monoxide-Nitrous Oxide Heterocycles

1 and 2 should be practical molecules preparable from phosgene [COCl₂] and hydroxyl or phosgene and Na₂N₂O₄!

Important idea:

3. Synthesis of 1-3 should be made major effort!!

These molecules also lead to study of the chemistry of N₂O₅, N₂O₄, BNO, and NBO!! These ideas will be developed further at OSU.

These are all new compounds being proposed by COX for study. They are in perfect CO₂ and N₂ balance --- and may be valuable as gasoline additive.
Compounds 1 and 2 are $E+2^-$ isomers. Compounds 3 and 4 are also attractive. The theory and calculations of the molecules on slides 10 and 11 are to be developed.
Polymerization of Nitrous Oxide

\[ \text{Na} \quad (1e) \quad \text{Na-N=N} \quad (1e) \quad \text{Na-N=N} \]

\[ \text{Na}[N=N-N=N]_n \quad \text{Na}[N=N-N=N]_{n+1} \quad 2 \text{ Cap} \quad [O] \]

Can \( \text{N}_2\text{O} \) and/or azides be polymerized or co-polymerized?

Can \( \text{N}_2\text{O} \) undergo cyclodimerization or cyclopolymerization?

\( \text{N}_2\text{O} \) adds to acetylenes to give \( \alpha,\beta \)-diesters. Can \( \text{N}_2\text{O} \) and acetylenes be co-polymerized?
Polymerization of Azides

\[
\begin{array}{c}
\text{N}≡\text{N}-\text{NF} \quad \xrightarrow{\text{Na} \ (1e)} \quad \text{Na-N=N} \quad \xrightarrow{n \text{ FN}_3} \\
\text{Na} \left[ \text{-N=N} \right]_n \quad \xrightarrow{\text{Na} \ (1e)} \quad \text{Na} \left[ \text{-N=N} \right]_{n+1} \quad \xrightarrow{\text{Cap} \ [O]} \\
\text{Cap} \left[ \text{-N=N} \right]_{n+1} + \left[ \text{-N=N} \right]_{n+1} \quad \text{Can azides be co-polymerized?}
\end{array}
\]

\[Z-\text{N}_3 = R_3\text{Si-N}_3, \text{O}_2\text{N-N}_3, \text{NC-N}_3, \text{F-N}_3\]

This will be of great significance if accomplishable. Such programs should be initiated. Active metals add to N\(_2\)O.
Stable [1,2,3]-Triazolo[1,2,3,4]tetrazines

Triazolotetrazine 2 is preparable and fairly stable. It is the only known stable 1,2,3,4-tetrazine and its chemistry should be determined. Tetrazine 2 cannot ring open to a bis-diag compound. The oxidation and deamination of 2 should be studied. The phenyl group in 2 should be replaced by a removable group.

Ohsawa, Chem. Comm., 1988
Oxidation of Hydrazones with Pb(OAc)$_4$.

Stabilizing groups are highly electron-attractive and conjugating: (e.g., esters, acid halides).

$\text{Pb(OAc)}_4 \xrightarrow{10-25 \, ^\circ \text{C}} \text{Pb(OAc)}_2 - 2 \text{HOAc}$

$\text{R}_2\text{C}=\text{N} \xrightarrow{\text{fast}} \text{R}_2\text{C}=\text{N}=\text{N} + \text{HOAc}$

The acetic acid produced during the reaction is also stabilizing (ca. 100%).

Non-hydrazone compounds are rapidly oxidized to monodene compounds by lead tetraacetate. Unless the diazo compounds are used rapidly to conjugate, they are decomposed very rapidly and irreversibly at their boiling point.

Most compounds of interest are developed from a source of synthetic diazo compounds, and the diazo compounds are not destroyed by the use of elevated temperatures.
Oxidation of Hydrazones with Pb(OAc)$_4$ in Tetramethylguanidine/Dimethylformamide

$$R_2C=\text{N-NH}_2 \xrightarrow{\text{Pb(OAc)}_4, \text{TMG, DMF, } -80 \, ^\circ\text{C}} R_2C=\text{N=N}$$

TMG = (CH$_3$)$_2$N-C-N(CH$_3$)$_2$; DMF = (CH$_3$)$_2$N-C-H


This method is the best known method for preparing monodiaz compounds at low temperatures. This method was originated and developed at Ohio State and published in 1995 as indicated. Of present interest and as proposed by DARPA/AIR FORCE is an extension of the method to vicinal-diazodihyrazones for practical syntheses of usable 1,2,3,4-tetrazines.

The TMG neutralizes the acetic acid and protects every diazo compound as yet prepared. Is the method usable for practical syntheses of vicinal diazo compounds? The DMF serves as an excellent solvent for alone reaction mixtures at low temperatures. The diazo compounds have been kept for days at -78°C.
Glyoxal Dihydrazones, Pb(OAc)$_4$, TMG, and CH$_2$Cl$_2$

\[
\begin{array}{c}
\text{H}_2\text{N} \quad \text{N} \quad \text{N} \quad \text{NH}_2 \\
\text{H-} \quad \text{C} \quad \text{C} \quad \text{H}
\end{array}
\xrightarrow{\text{Pb(OAc)$_4$}}
\begin{array}{c}
\text{N}_2 \quad \text{N}_2 \\
\text{H-} \quad \text{C} \quad \text{C} \quad \text{H}
\end{array}
\xrightarrow{-2 \text{N}_2}
\begin{array}{c}
\text{H} \quad \text{C} \equiv \text{C} \quad \text{H}
\end{array}
\sim 100\%

Reaction of glyoxal hydrazones with Pb(OAc)$_4$ occurs essentially instantly at temperatures as low as -120°C to give acetylene essentially quantitatively. It is not known if 1,3,3,4-tetrazine is actually produced in these experiments. These are problems in these very low temperature oxidations in that the reagents are not very soluble. The oxidations should be tried in liquid CO$_2$ at low temperatures. Vanadium oxidants should be investigated.
Of interest are the oxidative behavior of 1-amino-1,2,3-triazole with Pb(OAc)$_4$ in TMG at low temperatures. What is the behavior of 1-nitroso-1,2,3-triazole (1)? What is found is that 1 decomposes with loss of 2N$_2$ at < -85°C. The behavior shown is identical with that for physical diazene. dihydrozene in slide 19. 1,2,3,4-Tetrazine intermediates and intermediates and determine that reaction mechanism.

The system should be studied spectroscopically at low temperatures to better determine reaction mechanism.
Biacetyl Dihydrazones, Pb(OAc)$_4$, TMG, and CH$_2$Cl$_2$

\[
\begin{align*}
\text{H}_2\text{N}-&\text{N}-\text{N}-\text{NH}_2 \\
\text{CH}_3-\text{C}-\text{C}-\text{CH}_3
\end{align*}
\]

\[
\xrightarrow{\text{Pb(OAc)$_4$, TMG, CH$_2$Cl$_2$, -80 °C}}
\]

\[
\text{N}_2\text{N}_2
\]

\[
\text{CH}_3-\text{C}-\text{C}-\text{CH}_3
\]

Unstable

\[\xrightarrow{-2 \text{ N}_2}\]

\[
\text{CH}_3-\text{C}≡\text{C}-\text{CH}_3
\]

Unstable

Oxidation of biacetyl dihydrazones by Pb(OAc)$_4$ has been studied for preparation of 2,3-bis-diazopropene and for 5,6-dimethyl-1,2,3,4-tetrazine at low temperatures. In all present experiments, oxidation of 1 produces 2-butyne in >80% yield essentially instantly (on adding the Pb(OAc)$_4$). The structures of the actual intermediates in the above experiments are as yet unknown.
Oxidation of Vic-Dihydrazones with Pb(OAc)_4

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{N} \quad \text{N} \quad \text{NH}_2 \\
\text{R} - \text{C} - \text{C} - \text{R} \quad & \quad 2 \text{ Pb(OAc)}_4, \\
& \quad 0-25 \degree \text{C} \\
& \quad -2 \text{ Pb(OAc)}_2, \\
& \quad -2 \text{ HOAc} \\
\xrightarrow{\text{not detected}} & \quad \text{R} - \text{C} \equiv \text{C} - \text{R} \\
\end{align*}
\]

\[
\begin{align*}
\text{(CH}_2\text{)}_n & \quad \text{C} \Rightarrow \text{N-NH}_2 \\
& \quad 2 \text{ Pb(OAc)}_4, \\
& \quad 0-25 \degree \text{C} \\
& \quad -2 \text{ Pb(OAc)}_2, \\
& \quad -2 \text{ HOAc} \\
\xrightarrow{\text{not detected}} & \quad (\text{CH}_2\text{)}_n \quad \text{C} \equiv \text{N}_2 \quad \text{N}_2 \\
\end{align*}
\]

\[n = 3-8\]

This overhead summarizes the results of oxidizing open-chain and cyclic vicinal dihydrazones with Pb(OAc)_4, TMG, and CH_3Li. Aminobenzenes, even cyclopentynes, are produced in excellent yields. Of further interest is oxidation of 1,2-cyclooctatetraene dihydrazone with Pb(OAc)_4. Can cyclotetrayne be prepared? The strain in cyclotetrayne will be enormous!
Vic-Bis-diazo Compounds or 1,2,3,4-Tetrazines

Why are vic-diazo compounds so unstable whereas mono-diazo compounds aren't? Is stereochemistry very important? Are the 2 positive charges on adjacent carbon making the vic-diazo compounds so unstable? These results are very surprising.
Synthesis of Tetrazine 1,3-di-N-oxides

\[
\begin{align*}
\text{1} & \xrightarrow{-80^\circ C} [O] \rightarrow \text{3} \\
\text{2} & \xrightarrow{-80^\circ C} [O] \rightarrow \text{4}
\end{align*}
\]

Study was initiated of possible oxidative conversion of 1 and 2 to 3 as a possible practical source of 4. The oxidizing agent 5 is much more powerful

\[ [O] = \text{Pb(OAc)}_4/\text{TMG}; \text{Pb(O}_2\text{CCF}_3)_4/\text{TMG} \]

and can be used at lower temperatures than 5.
Oxidation of o-Quinone Dihydrazones with Pb(OAc)$_4$

Investigation: Lower Temperatures; Solvents; IR; Oxidants; Traps

Oxidation of 1 Pb, Pb(OAc)$_4$/TMG at temperatures as low as -100°C yields biphenylene (≈80%) and 1,4-dicyanoundecadiyne (≈20%). Benzodiazepine could not be detected. Can the oxidation be affected at lower temperatures?
Of interest is the oxidative behavior of 1-aminobenzotriazole. Will the products of reaction of 1 be the same as in the previous overhead? The results are essentially identical; tetrazine 2 has as yet not been detected. Of note is that 1,4-dicyano-1,3-butadiene is formed.
Of interest is the oxidative behavior of 2-aminobenzotriazole. It has been presently found that oxidation of 2-aminobenzotriazole gives much more dicyano-1,3-benzenedione than does 1-aminobenzotriazole. The reaction intermediates are different.
Oxid’n of Acenaphthenequinone Dihydrazones with Pb(OAc)$_4$

Of interest is oxidation of its a stable bis-diazo compound 2, a stable 1,2,3,4-tetrazine 3, a stable acenaphthene 5 and/or a product which might be converted to a simple tetrazine 1,3-din oxide 6. The facts: oxidation of 1 gives 4, a vicinal bis-dinitrile in >90% yield.

Investigation: Oxidants, Temperature, Solvents, Structures
Furazanotetrazine 4,6-Di-N-oxide (FTDO)

FTDO is now the desired because it is proposed to be usable for preparing 1,3-DDO and 1,3-DDTO.

FTDO was synthesized in the early 70s and was minimally described in a dissertation. The synthesis of FTDO is in a Ph.D. Thesis in Arizona. I want a copy of the Thesis.

We will spend a lot of time on preparation of FTDO.

FTDO is needed in large quantity!

The mechanism of this reaction is not known.

There are no X-ray data for this product.

The nitramine is first generated which then loses OH to give the intermediate below.

FTDO is minimally described in the paper cited.

It is possible that the method described in the paper was not correct.

The melting point for FTDO is 110-113°C.

Careful reading of this paper raises problems as to how reliable the Russian synthesis is.

Churakov et al, Tetrahedron, 1995

The method for preparing FTDO in Russia that has described much later for longanitrazine 1,3-di-N-oxide.
Furazanotetrazine 4,6-Di-N-oxide (FTDO)

This is a summary of the Russian and now a OSIR synthesis of FTDO. Preparation of FTDO has been difficult: the CIA has somebody should have scanned a Russian thesis describing the final steps in the synthesis.

Furazanotetrazine 4,6-Di-N-oxide (FTDO)

\[
\begin{align*}
\text{H}_{2}\text{NOH} + \text{HCl} & \xrightarrow{\text{NaOH}, \Delta} \text{H}_{2}\text{N} - \text{C} - \text{C} - \text{NH}_{2} \\
\text{N} & \xrightarrow{\text{Na}_{2}\text{WO}_{4}, \text{H}_{2}\text{SO}_{4}, 30\% \text{H}_{2}\text{O}_{2}} \text{N} - \text{C} - \text{N}=\text{O} \\
& \xrightarrow{\text{ButNBBr}_{2}, \text{CH}_{3}\text{CN}} \text{N} - \text{C} - \text{no = Bu}^{+} \\
& \xrightarrow{-\text{Bu}^{+}} \text{O} - \text{N} = \text{C} - \text{C} - \text{N} = \text{N}=\text{O}
\end{align*}
\]

There have been problems in this step! To scale up this step satisfactorily is questionable.

We like \(\text{Na}_{2}\text{SO}_{4} \cdot \text{BF}_{3}\) much better than \(\text{Na}_{2}\text{BF}_{4}\) at present.

X-ray analysis of FTDO has not been successful. The crystals have not been satisfactory!
The following transformations of FTDO have not been successful. These reactions are believed to being investigated in Moscow. This study needs much stronger support and should be discussed in much greater detail. Where are the Russians in these areas?

If 1 can be prepared as indicated, this approach to synthesis of DTO and IsoDTO could be practical.

Acid- and base-catalyzed hydrolyses of FTDO give many products.

This is an important project! We have not had sufficient support to investigate the above project properly. "Zelinski" has had a 10-12 year head start on this work.
This overhead summarizes the present route proposed for DTTO YOX.
Are the Russians studying this route? We believe so.

Proposed Synthesis of DTTO

\[
\begin{align*}
\text{N=N=N-But} & \quad \text{NO}_2\text{BF}_4 \quad \text{H}_2\text{O}, \quad -\text{H}_2\text{O}, \quad -\text{BF}_4^- \\
\text{N=N=N-But} & \quad \text{N=N=N-But} \\
\end{align*}
\]
Proposed Synthesis of IsoDTTO

This synthesis of IsoDTTO parallels that for DTTO on the previous overhead. The key is successful ring-opening of FTDO!
Proposed Synthesis of DTTO

This is an alternate synthesis of DTTO. This ring-closure is different than that proposed previously. This sequence also proposes initial preparation of a 1,2,3,4-tetraguanine tetraoxide which is stable.
Furazanotetrazine 1,3-Di-N-Oxide

\[
\begin{align*}
\text{Furazanotetrazine 1,3-Di-N-Oxide} \\
\text{OHIO STATE} \\
\text{This is a major advance in synthesis of FTDO!}
\end{align*}
\]
Synthesis of Triazolotetrazine 1,3-Dioxides

\[
\begin{array}{cc}
\text{Z-N} & \text{N} \\
\text{N} & \text{N} \\
\text{N} & \text{N} \\
\text{N} & \text{N} \\
\text{N} & \text{N} \\
\text{N} & \text{N} \\
\end{array}
\]

Z = H, SiR\text{\textsubscript{3}}, R-SO\text{\textsubscript{2}}, R-C, CN

Are these sequences being investigated interested?

These synthesis routes are now to be studied. This effort will have to be funded soon. Very practical chemistry might come from these sequences. Ab initio sequences have been initiated at CSU.
Possible Synthesis of DTTO

This molecule should be readily prepared. A major contribution! To be emphasized is that only isomers at N5, and N7 are of interest.

A possible practical synthesis of DTTO as yet not investigated. This is a major and important project. To be discussed further if possible.
Synthesis of Benzotetrazine 1-N-Oxide

This overhead illustrates the first publication by Zelinsky for synthesis of a stable benzotetrazine oxide.

\[ \begin{align*}
\text{NH}_2 & \quad \text{HNO}_2, \text{BF}_3 \\
\text{N}_2^+\text{BF}_4^- & \quad \text{Bu}_t\text{F}, \text{BF}_3
\end{align*} \]

We know little about o-nitroso azides.

This is an important concept. Various heterocyclic (5 and 6-membered ring) o-nitroso azides should be evaluated. Do the molecules proposed exist in ring-open or ring-closed forms?

fairly stable
Synthesis of Benzotetrazine 1,3-Di-N-oxide

\[
\begin{align*}
\text{N}=\text{O} & \quad 1. \text{Bu}_t\text{NBr}_2 \\
\text{NO}_2 & \quad 2. \text{SnCl}_2, \text{H}_2\text{O} \\
\text{NH}_2 & \quad \text{N}_2\text{O}_5 \\
\text{mp 177-179°c} & \quad \text{Very stable}
\end{align*}
\]

Churakov, Mendel. Comm. 1991

This is a very important paper that was ignored in the US.

This publication extends and improves the previous methodology for preparing benzotetrazene 1,3-di-N-oxides.
Synthesis of Benzotetrazine 1,3-Di-N-oxide

an improved synthesis of benzotetrazine 1,3-di-N-oxide

\[
\text{NO}_2 \xrightarrow{\text{Bu}_t \text{NBr}_2} \text{HN}^+\text{N}^- \xrightarrow{\text{SnCl}_2, \text{H}_2\text{O}} \text{N}^+\text{N}^-\text{Bu}_t
\]

\[
\text{NO}_2 \xrightarrow{-\text{Bu}_t \text{O}_3\text{SCF}_3} \text{N}^+\text{N}^-\text{N}^+\text{N}^-\text{O}^- \xrightarrow{\text{O}_2\text{NO}_3\text{SCF}_3} \text{N}^+\text{N}^-\text{Bu}_t
\]

Nitronium triflate is generated from \((\text{CH}_3)_3\text{N}^+\text{NO}_2^-\) and \((\text{CF}_3\text{SO}_2)_2\text{O}\); the Schildklotz method.

Ohio State, 2003

The major contribution of OSU is use of nitronium triflate.
Benzotetrazine 1,3-Di-N-oxide

A new method for preparing benzotetrazine 1,3-di-N-oxide

\[
\begin{align*}
\text{NO}_2 & \quad \text{(CH}_3\text{)}_3\text{SiCl} \quad \text{Et}_3\text{N} & \quad \text{NO}_2 \\
\text{NH}_2 & \quad \text{NH-Si(CH}_3\text{)}_3 & \quad \text{NH-Si(CH}_3\text{)}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{N}=\text{N}-\text{Bu}_t & \quad 1. \text{60}^\circ \text{C} \quad 2. \text{NH}_4\text{Cl} \quad \text{H}_2\text{O} & \quad \text{N}=\text{N}-\text{Bu}_t \\
\text{NH-Si(CH}_3\text{)}_3 & \quad & \quad \text{NH}_2 \\
\end{align*}
\]

\[
\begin{align*}
\text{N}=\text{N}-\text{Bu}_t & \quad \text{PCl}_5 & \quad \text{N}=\text{N}-\text{Bu}_t \\
\text{NH-NO}_2 & \quad & \quad \text{N}=\text{N}-\text{Bu}_t \\
\end{align*}
\]

\[
\begin{align*}
\text{NO}_2\text{BF}_4 & \quad (\text{O}_2\text{N-})_2\text{Si-}\text{CF}_3 & \quad \text{nitronium triflate is a superb initiating agent.}
\end{align*}
\]

**OHIO STATE**

A good method developed by Dr. Venugopal for preparing benzotetrazine 1,3-di-N-oxide.
Substituted Benzotetrazine 1,3-di-N-oxides

The $E_1$ and the $E_2$ substituted benzotetrazines undergo accelerated displacement by various nucleophiles. The behavior of N-substituted benzotetrazine 1,3-di-N-oxides are similar to that of pyridyl bromide and 1-fluoro-2-nitrobenzene.

$E^+ = X^+, \text{NO}_2^+, \text{SO}_3^-$; $\text{Nuc}^- = \text{RO}^-, \text{RS}^-, \text{R}_2\text{NH}$, etc.

$\text{Nuc}^- = \text{OH}, \text{Ac}, \text{OS}, \text{R}_3$, and $\text{NH}_2$ as displacement nucleophiles have not been reported by Hocaw.
Synthesis of 1,2,3,4-Tetrazine-1,3-di-N-oxides

The following displacements and subsequent reactions are principal present objectives. At present, many different oxidizing agents might have to be studied.

Can mono-1,2,3,4-tetrazine-1,3-di-N-oxides be prepared? Are they sufficiently stable for subsequent use for synthesis of DTTO and/or ISO-DTTO? The fundamental physical-organic chemistries of such metrical need determination.
These reactions have been studied at CSEU. They work well and the products are readily separated and quite stable. Present results agree with that communicated by Moscow!
These reactions are being studied at OX1. Reaction 1 occurs as expected.
Reaction 2 using KOH at 100°C occurs surprisingly to give the indicated triangle.
Reaction 3 at 25°C occurs well. This low-temperature reaction will be studied later.
Synthesis of 1 and/or 2 are now being studied. Oxidations of 1 and 2 to quinone 3 or otherwise are to be investigated. Will the 1,2,3,4-tetrazine-1,3-di-N-oxide ring system stay intact?
The low temperature behaviors of 1 with OH and with NH₂ are being studied at ORNL at present. The products indicated are to be oxidized in effort to prepare 1,3,4-triazine-1,3-di-N-oxide derivatives, usable for preparation of OTTO and/or ISOOTTO.
Reaction of benzotriazole-1,3-di-N-oxide with hot KOH to give benzotriazole with expulsion of KNO₃ is unexpected. The effects of temperature on the basic system are to be determined.
o-Quino-1,2,3,4-tetrazine 1,3-Dioxide (QTDO)

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{NH-OH} \quad \xrightarrow{[O]} \quad \text{H}_2\text{N} & \quad \text{N=O} \\
\text{O} & \quad \text{C} & \quad \text{C} & \quad \text{O} \\
\text{O} & \quad \text{C} & \quad \text{N=O-But} & \quad \text{NO}_2\text{BF}_4
\end{align*}
\]

\[
\begin{align*}
\text{O} & \quad \text{C} & \quad \text{N=O-But} & \quad \text{NO}_2\text{BF}_4 \\
\text{O} & \quad \text{C} & \quad \text{NH-NO}_2 & \quad \xrightarrow{\text{NO}_2\text{BF}_4} \\
\text{O} & \quad \text{C} & \quad \text{NH}_2
\end{align*}
\]

\[
\begin{align*}
\text{O} & \quad \text{C} & \quad \text{N=O-But} & \quad \xrightarrow{\text{NO}_2\text{BF}_4} \\
\text{O} & \quad \text{C} & \quad \text{N=O-But} & \quad \xrightarrow{\text{NO}_2\text{BF}_4} \\
\text{O} & \quad \text{C} & \quad \text{N=O}
\end{align*}
\]

QTDO may be a cheap precursor to DTDO or and/or DTDO. Synthesis of QTDO as above has been proposed to DARPA/ARPA.

QTDO is of interest as an energetic material and, in gasoline, etc., as a practical source of N₂O.
Possible Synthesis of Pentazine N-Oxides

Pentazine N-Oxides are unknown; azido-oxides should be stable, highly interesting new structures; the following sequence involves new reaction schemes:

\[ Z-\text{CH}_2-\text{N}=\text{N}-\text{SiMe}_3 \xrightarrow{[\text{O}]} Z-\text{CH}_2-\text{N}=\text{N}-\text{SiMe}_3 \]

1. BuLi
2. TosN\(_3\)

\[ Z-\text{C}^++\text{N}=\text{N}-\text{SiMe}_3 \xrightarrow{\text{NOBF}_4^-} \]

\[ Z-\text{C}^-\text{N}=\text{N}-\text{SiMe}_3 \]

\[ \text{N}_2 \]

\[ \text{N}^- \]

\[ \text{N} = \text{O} \]

\[ \text{F}^- \]

\[ \text{O}^- \]

\[ \text{N} = \text{O} \]

Z = H, R, Ar, NO\(_2\), CN, RO, X, etc.
Proposed Synthesis of Tetrazine 1,3-Di-N-oxides

Vary $X, Y, R_3Si$ and Oxidant

![Chemical structures and reactions](image)
Synthesis of Cyanogen N,N'-dioxide

\[
\begin{align*}
\text{O} & \equiv C - C \equiv N - O^- \\
\text{H} & \text{H} \\
\text{Cl} & \text{Cl} \\
\text{Cl} & \text{Cl}
\end{align*}
\]

Major programs involving cyanogen N,N'-dioxide for synthesis of energetic materials may be envisaged.
Synthesis of IsoDITTO

2 B: -2 HCl

2 NaN₃ -2 NaI

2 [O]

The oxidizing agent will have to be selected.

Nothing is known of the behaviour of iso-azidinitriles ON stability.

Do they end...
Possible Synthesis of IsoDTTO

This synthesis of IsoDTTO has not been investigated as yet. Successful IsoDTTO will be inexpensive!
Possible Synthesis of DTTO

Br₃C-C\(\text{NOH}\)\n\xrightarrow{\text{Ag}_2\text{O}}\ Br₃C-C\(\text{N=O}\)

LDA \(ightarrow\) HBr

\(\text{N}_3\text{C}=\text{C}\text{N}=\text{O}\)\n\xrightarrow{2 \text{NaN}_3\ -2 \text{NaBr}}\ \text{BrC}=\text{C}\text{N}=\text{O}

Again, do res- azidoazides ring close to tellurium-mono-N-oxides?

major programs based on 1,1-dinitro-1,1-dinitromethyl hydride should be carefully evaluated.

\(\text{N}_3\text{C}=\text{C}\text{N}=\text{O}\)\n\xrightarrow{[\text{O}]}\ \text{N}_3\text{C}=\text{C}\text{N}=\text{O}
This sequence was developed by Baum at Fluorochem and by Alekseeva at OSU.

Baum; Alekseeva

A very interesting method prepared Part which has not been studied further.
Possible Synthesis of DTTO

\[
\begin{align*}
\text{N=O} & \quad \text{N=O} \\
\text{N}_3 & \quad \text{N}_3 \\
\text{C} & \quad \text{C} \\
\text{C} & \quad \text{C} \\
\text{I} & \quad \text{I} \\
\text{2 NaN}_3 \quad \overset{\text{2 NaN}_3}{\overset{\text{2 NaN}_3}{\text{-2 NaI}}} & \quad \overset{\text{[O]}}{\text{[O]}} \\
\text{N=O} & \quad \text{N=O} \\
\text{C} & \quad \text{C} \\
\text{C} & \quad \text{C} \\
\text{I} & \quad \text{I} \\
\end{align*}
\]

Major programs on use of tetraiodoethylenine, triiodoethylene, and diiodoethylene should be evaluated.
Possible Synthesis of IsoDTTO

Reactions of diiodoacetylene and $\text{NaN}_3$ (and other nitroxylic agents) are being studied on a DARPA program at Ohio State.