Development of Solventless Nitration Processes Using *tert*-Butyl Nitrite

WP-2750

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NSWC IHEODTD

9 May 2019

SERDP
DOD ▪ EPA ▪ DOE

Distribution A: Approved for Public Release (Log # 18-235)

Project Team

- PI: David T. Boruta, Ph.D.
- HPLC Analytics: Aaron S. Jenkins

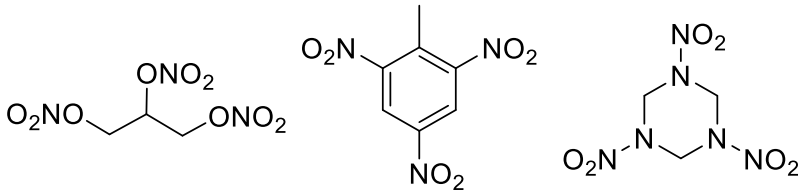
Acknowledgements:

- Kirsten F. Warner, Ph.D. – Was involved right when the project started, but then took a position at DDESB.

Background & Technical Objectives

FY17 Statement of Need (SON) called for by SERDP was focused on developing solventless nitration processes to known energetic ingredients under a SEED effort.

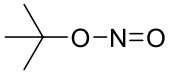
- Need for new, more environmentally friendly processes to nitroglycerin, trinitrotoluene and RDX.
- Solvent recycling options were discouraged.



NG **TNT** **RDX**

Targets called for under the FY17 SERDP SON for Solventless Nitration

The Chemical Scale-up Group at NSWC IHEODTD proposed to this effort to expand upon existing reported nearly solventless nitrations reported in the literature using *tert*-butyl nitrite.



***tert*-Butyl Nitrite**

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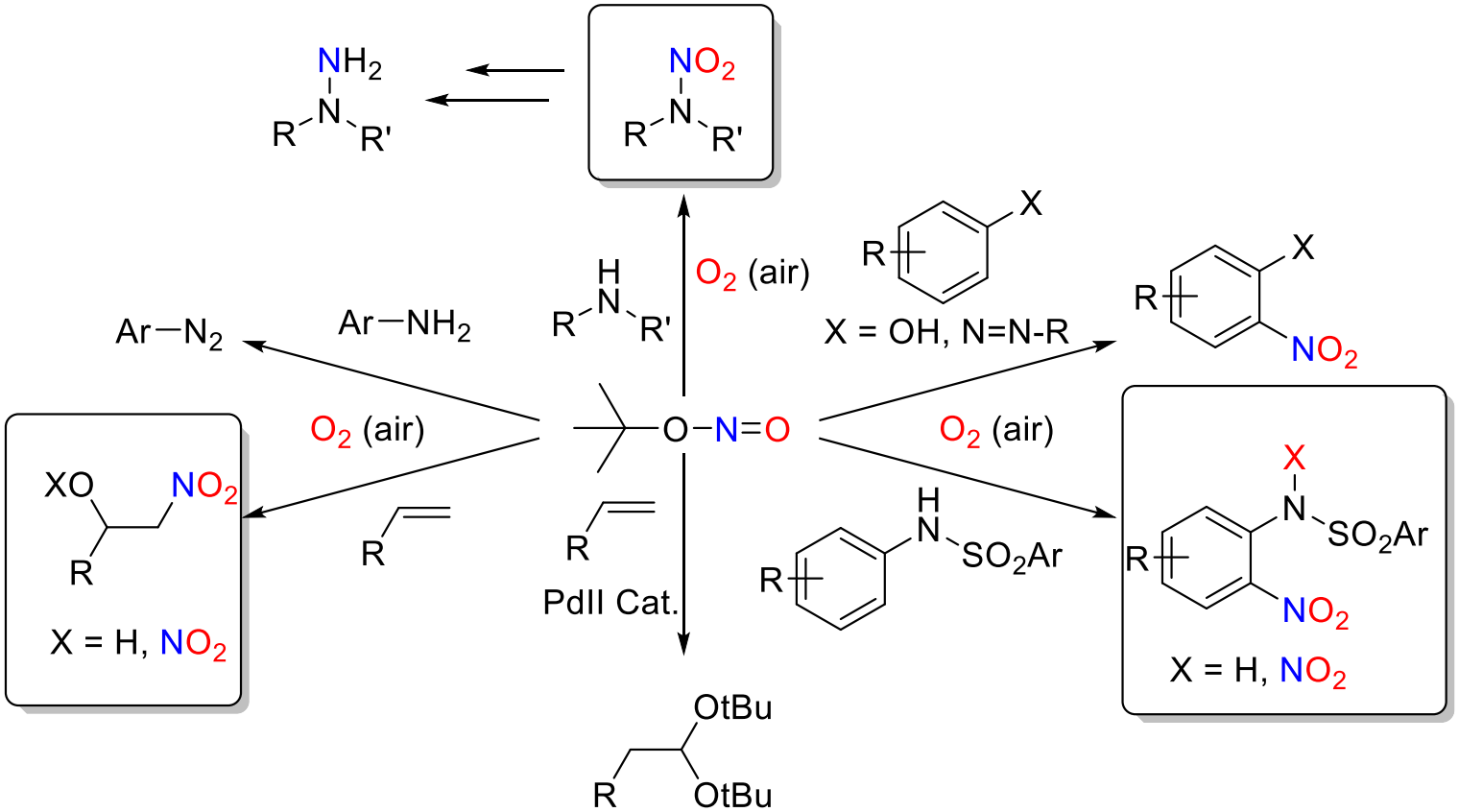
Technical Approach



Various reported reactions of *tert*-butyl nitrite in the open literature

Technical Approach

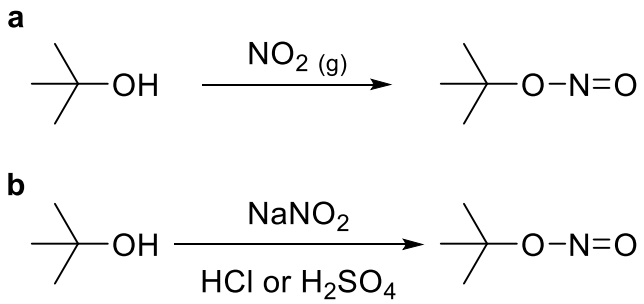
1950: Patent application filed for the synthesis of *tert*-butyl nitrite from *tert*-butanol and NO_2 gas.

1955: DuPont files patent application for large continuous feed *tert*-butyl nitrite synthesis from *tert*-butanol and NO_2 generated from the oxidation of ammonia gas.

1980's: Laboratory scale prep of *tert*-butyl nitrite from Sandmeyer reaction.

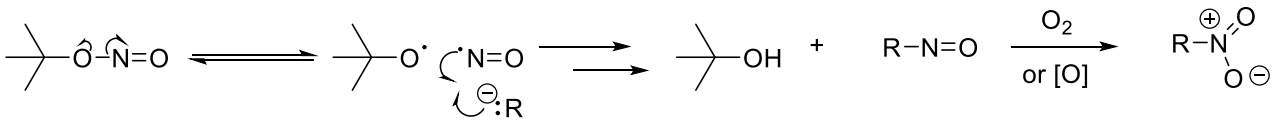
1990: Patent application filed for Sandmeyer process.

2011: Continuous flow Sandmeyer process developed collaboratively by University of Ghent (Belgium), Corning (France), and BIOS Chemicals (France).



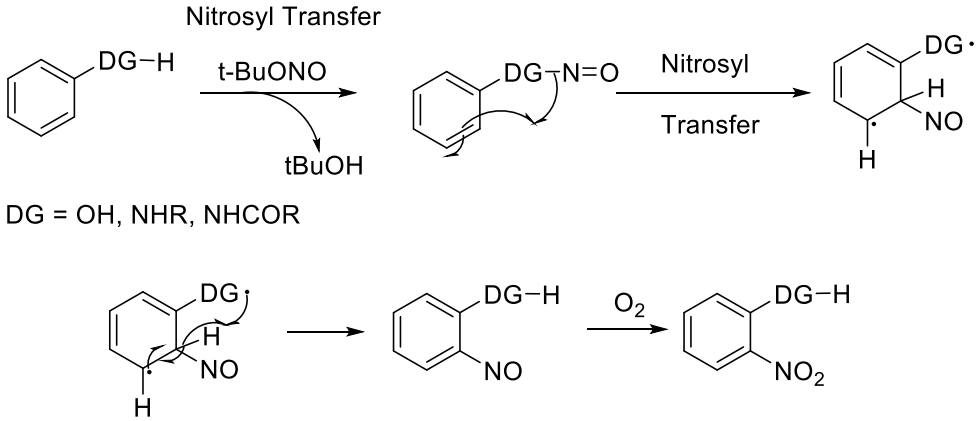
The two industrial syntheses of *tert*-butyl nitrite

Technical Approach



R = alcohol, 2° amine, alkene, arene

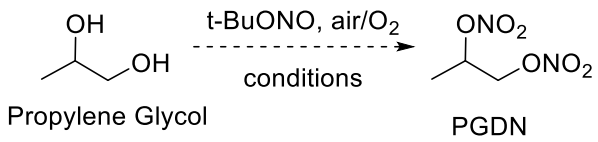
The understanding of *tert*-butyl nitrite's reactivity at the beginning of this effort.

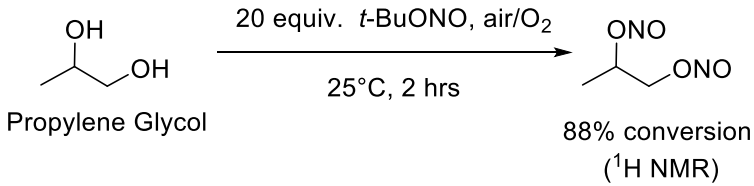


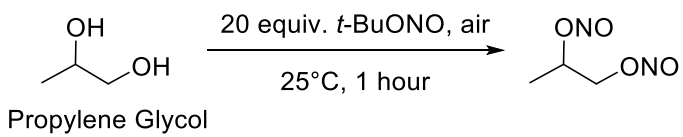
DG = OH, NHR, NHCOR

The understanding of directed nitration using *tert*-butyl nitrite at the beginning of this effort.

Attempted Nitrate Ester Synthesis







Attempts to Synthesize PGDN instead of Dinitroso-propylene Glycol		
Entry	**Reaction Conditions**	**PGDN Detectable by HPLC?**
1	Add H_2O, 15°C, O_2 purge, 5 hrs	No
2	Add H_2O, 15°C, open air, 5 hrs	No
3	15°C, O_2 purge, 5 hrs	No
4	3 Equiv. *t*- BuONO, add H_2O, 20°C, O_2 purge, 5 hrs	No
5	1.3 equiv. PG, 1 equiv. *t*- BuONO	No
6	1.5 equiv. PG, 1 equiv. *t*- BuONO	No
7	2.0 equiv. PG, 1 equiv. *t*- BuONO	No

Conversion optimization screening

Entry	Equiv. tBuONO	Temp. (°C)	Time (hrs)	%Conv. (NMR)
1	3	0	2	20
2	3	0	20	22
3	3	30	2	22
4	3	30	20	26
5	3	40	2	26
6	3	40	20	31
7	11.5	0	15	65
8	11.5	15	11	66
9	11.5	30	2	54
10	11.5	30	11	56
11	11.5	30	20	58
12	11.5	40	15	63
13	20	0	2	82
14	20	0	20	84
15	20	30	2	88
16	20	30	20	93
17	20	40	2	78
18	20	40	20	72
19	**20**	**15**	**1**	**68**
20	**20**	**15**	**1**	**76**

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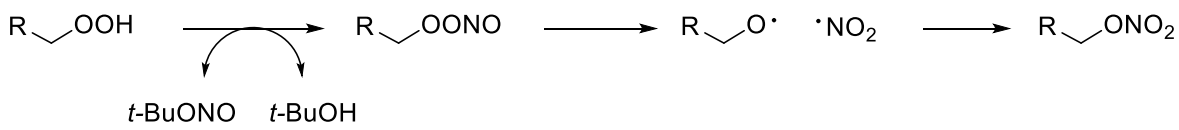
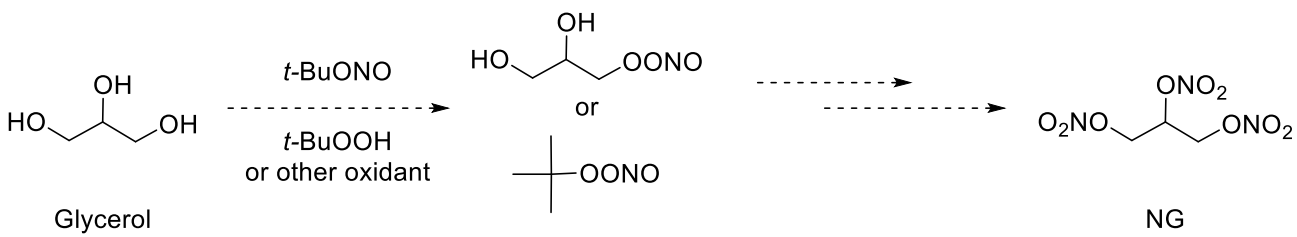
New Possible Path to Nitrate Esters?

Mechanism put forth by Bag, et. al.

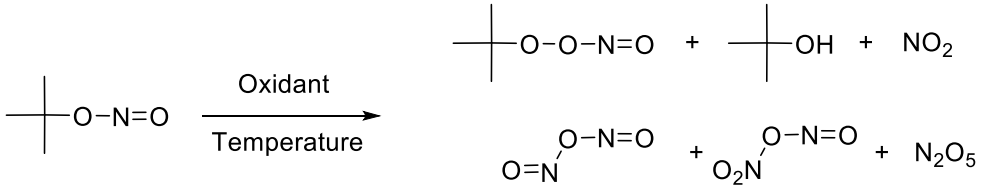


Bag, R.; Sar, D.; Punniyamurthy, T. *ACS Omega*, **2017**, *2*, 6278-6290

Proposed possible pathway to nitroglycerin in this effort



Oxidant Compatibility



Plausible reaction products

Oxidant Compatibility with *tert*- Butyl Nitrite			
Entry	**Oxidant**	**Temp. (°C)**	**Observations**
1	50% H_2O_2	25	Violent decomposition & fume-off
2	50% H_2O_2	8	Violent decomposition & fume-off
3	20% H_2O_2	25	Bubbling/gas generation
4	20% H_2O_2	8	Bubbling/gas generation
5	70% *t*- BuOOH	25	Exotherm, gas generation, green color
6	70% *t*- BuOOH	8	Milder exotherm, clear
7	Urea · H_2O_2	25	No solubility; no reaction
8	Oxone	25	No solubility; no reaction
9	$K_2S_2O_8$	25	No solubility; no reaction
10	TEMPO	25	Orange color, yellow precipitate

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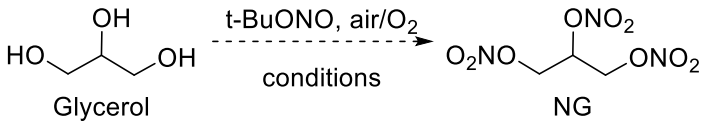
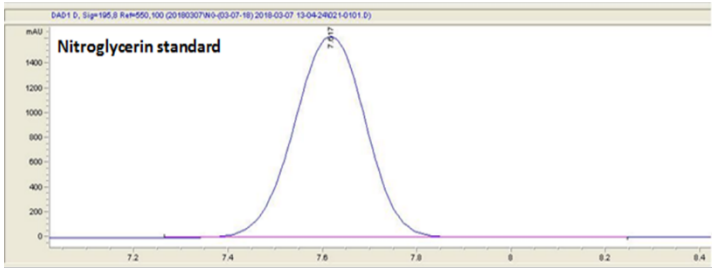
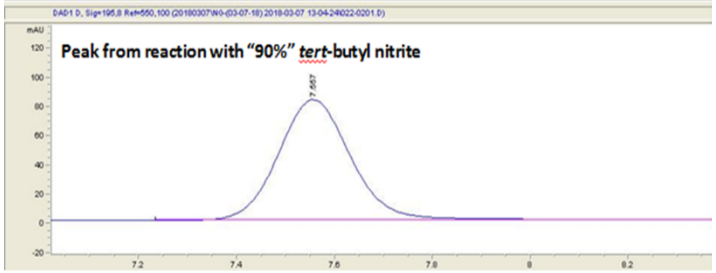
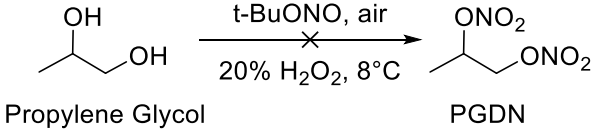
Renewed Attempts Toward NG/PGDN

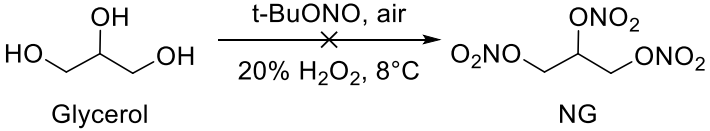


Reaction of Glycerol with *t*-BuONO		
Entry	**Reaction Conditions**	**Result**
1	20 equiv. *t*- BuONO, 25°C	Nitrosation products
2	3.5 equiv. *t*- BuONO; 3.5 equiv. 70% *t*-BuOOH 5°C	Nitrites (major), Nitrate ester (minor, small)
3	**2**, adding glycerol to *t*- BuONO/*t*- BuOOH mixture	Nitrites (major), Nitrate ester (minor, small)
4	**2**, adding *t*-BuONO to glycerol/*t*-BuOOH mixture	White polymer
5	**2**, add excess *t*-BuOOH	Decomposed material
6	5.00 equiv. *t*-BuONO ("90%") 25°C, air	Nitrites (major), Nitroglycerin (minor, NMR)
7	5.00 equiv. *t*-BuONO ("90%") 25°C, O_2	Nitrites (major), Nitroglycerin (minor, NMR/HPLC)
8	5.00 equiv. *t*-BuONO ("90%") 40°C, O_2	Nitrites (major), Nitroglycerin (minor, NMR/HPLC)
9	3.5 equiv. *t*- BuONO; 5 mol% $Cu(HFAcAc)_2$ 25°C	Nitrites; no nitrate ester
10	3.5 equiv. *t*- BuONO; 5 mol% $Cu(NO_3)_2$ 25°C	No product









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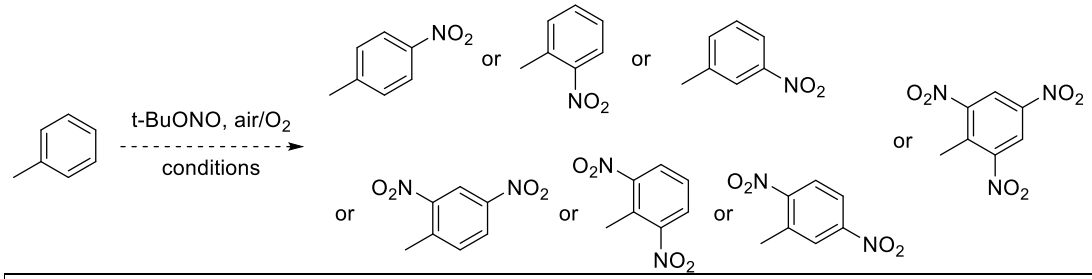
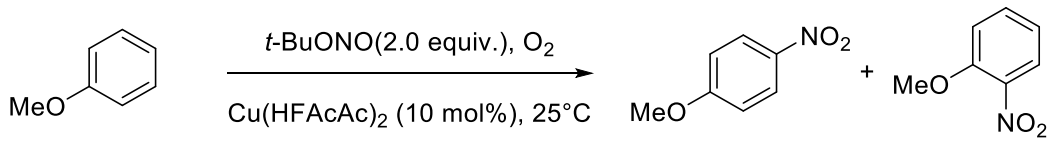
Toluene Nitration Development



Screen: Reaction of Toluene with *tert*- Butyl Nitrite (all reactions under O_2 purge)				
Entry	**Equiv. tBuONO**	**Temp. (°C)**	**Catalyst/Additive**	**Result**
1	up to 20	20	None	No reaction
2	up to 20	40	None	No reaction
3	up to 20	60	None	No reaction
4	up to 20	25	H_2O (3.00 equiv.)	No reaction
5	10	60	H_2O (5.00 equiv.)	Oxime (<10%)
6	20	25	3 mol% $CuBr_2$	No reaction by TLC or NMR
7	20	25	3 mol% $CuCl_2$	Complex product mixture (<10%, NMR)
8	20	25	3 mol% TEMPO	Mixture of products (<5%, NMR)
9	20	50	3 mol% $CuCl_2$	Complex product mixture (<10%, NMR)
10	10	20	3 mol% TEMPO (air)	Mixture of products (<5%, NMR)
11	10	20	3 mol% TEMPO	Mixture of products (<5%, NMR)
12	10	20	TEMPO (3.00 equiv)	No desired products (NMR)
13	3	60	30 mol% $CuCl_2$	No product by TLC
14	3	60	30 mol% $Cu(AcAc)_2$	No product by TLC
15	3	60	30 mol% Cu(Trifluoro-AcAc)$_2$	No product by TLC
16	3	60	30 mol% Cu(Hexafluoro-AcAc)$_2$	Mono-nitration by TLC, NMR (<25% yd), possibly Di-
17	3	60	30 mol% $Pd(dba)_2$	No product by TLC
18	3	60	30 mol% $Pd(OAc)_2$	No product by TLC
19	3	60	30 mol% $Ni(AcAc)_2$	Mono-nitration by TLC, mixture by NMR (10% yd)
20	3	60	10 mol% $NiCl_2$	No product by TLC
21	3	60	10 mol% $Ni(AcAc)_2$	No product by TLC
22	3	60	10 mol% $Ni(AcAc)_2$, 10 mol% BiPy	Reaction on the ligand by NMR
23	3	60	10 mol% $Ni(AcAc)_2$, 10 mol% BrettPhos	Reaction on the ligand by NMR
24	3	60	10 mol% $Cu(NO_3)_2$	Reaction by TLC; complex mixture by NMR, (<5%)
25	3	60	10 mol% $Cu(HFAcAc)_2$	Mono- & Di-nitration by TLC, NMR (<20% yd)
26	3	60	10 mol% $Cu(HFAcAc)_2$, 10 mol% BiPy	No product by TLC
27	3	60	10 mol% $Cu(HFAcAc)_2$, 10 mol% Brettphos	No product by TLC
28	6	60	10 mol% $Cu(HFAcAc)_2$	Mono- & Di-nitration by TLC, NMR (<20% yd)*

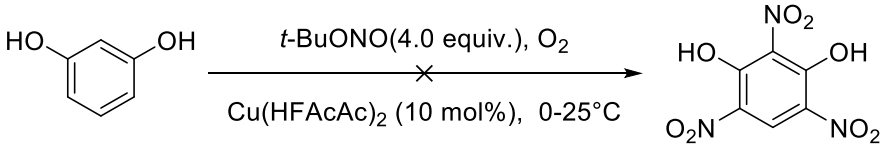
Attempted Scope Expansion

Attempted nitration of Anisole



Major products confirmed via co-elution by TLC with authentic standard

Attempted nitration of Resorcinol



Runaway reaction both with and without catalyst.
Only decomposition products observed even at 0°C.

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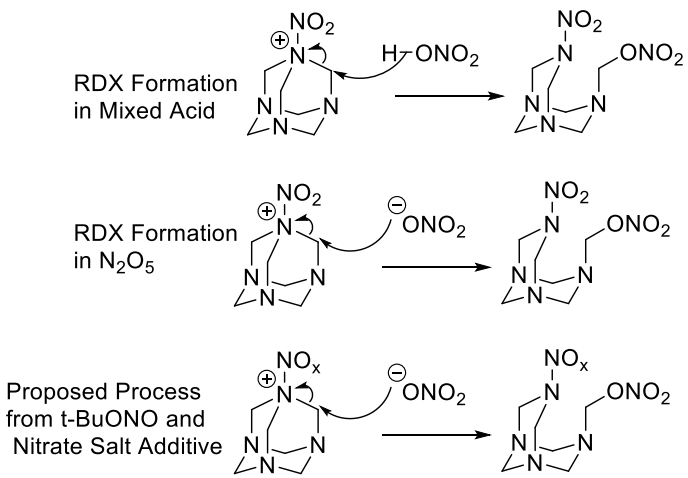
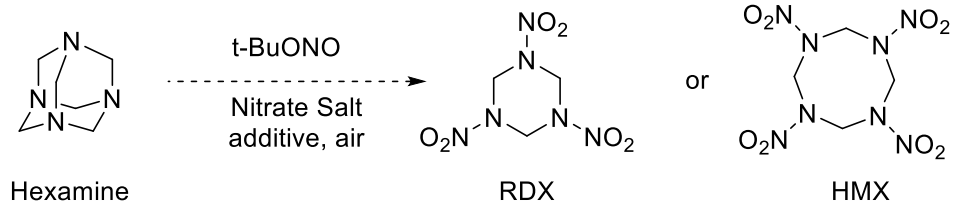
Reaction of Hexamine with *t*-BuONO





Solubility was determined to be a major issue for this reaction. Some reactivity was observed when acetonitrile was added.

Attempted Nitrosative/Nitrative Cleavage of Hexamine				
Entry	**Equiv. tBuONO**	**Temp. (°C)**	**Catalyst/Additive**	**Result**
1	6	20	None	No reaction by NMR
2	6	60	None	No reaction by NMR
3	6	25	Sodium Nitrate	No reaction by NMR
4	6	25	$NaNO_3$+ H_2O	Partial ring opening by NMR (<10% yd)
5	6	25	$NaNO_3$+ MeCN	Trace reaction by NMR
6	6	25	$NaNO_3$+ DMF	No reaction by NMR
7	6	25	$NaNO_3$+ DMSO	Trace reaction by NMR
8	6	25	NMe_4NO_3	No reaction by NMR
9	6	25	NMe_4NO_3 + MeCN	Partial ring opening by NMR (<10% yd); traces of RDX + HMX by NMR
10	6	25	$Cu(NO_3)_2$	No reaction by NMR
11	6	25	$Cu(NO_3)_2$ + MeCN	Partial ring opening by NMR (<10% yd); RDX present by NMR
12	6	25	$AgNO_3$	No reaction by NMR
13	6	25	$AgNO_3$ + MeCN	Partial ring opening by NMR (<10% yd); RDX present by NMR

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Key Points

Nitrate Esters

- Major product: Nitrosation of alcohols *via* nitrosyl transfer.
- Report from Bag, *et al* confirms our observations that the reaction with alcohol only results in nitrosyl transfer.
- Reproducibly synthesized nitroglycerin in trace amounts using 90% "Reagent Grade" *tert*-butyl nitrite from Sigma-Aldrich.
- Considering possibility that this grade reagent contains NO_X or peroxynitrite impurities.
- **Take-Away: Only works in trace amounts.**

Nitroarenes

- Achieved nitration of unactivated arene, toluene, using a copper(II) catalyst.
- Scope expanded to nitration of anisole; only initial results.
- **Take-Away: Yields are too low to be useful currently.**

Reaction with Hexamine

- Solventless nitration/nitrosation of hexamine severely hindered by solubility issues.
- Trace reactivity observed when acetonitrile used as co-solvent.
- **Take-Away: Reaction is possible, but not without solvent.**

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Technology Transfer & Bibliometrics

- Conference Presentations:
  - Boruta, D.T.; Jenkins, A. S. "Development of Solventless Nitration Processes Using *tert*-Butyl Nitrite," *JANNAF 45th SMBS/41st PEDCS/30th SEPS/PIB Joint Subcommittee Meeting,* Vancouver, WA, December 2018.
- Conference Posters:
  - "WP2750: Development of Solventless Nitration Processes Using *tert*-Butyl Nitrite," David T. Boruta, Aaron S. Jenkins. *SERDP ESTCP Symposium*, Washington, DC, November 28, 2018.
  - "WP2750: Development of Solventless Nitration Processes Using *tert*-Butyl Nitrite," David T. Boruta, Aaron S. Jenkins, and Kirstin F. Warner. *SERDP ESTCP Symposium*, Washington, DC, November 29, 2017.
- Conference Proceedings:
  - Boruta, D.T.; Jenkins, A. S. "Development of Solventless Nitration Processes Using *tert*-Butyl Nitrite," *Proceedings of the JANNAF 45th SMBS/41st PEDCS/30th SEPS/PIB Joint Subcommittee Meeting,* Vancouver, WA, 2018.
- Government Reports:
  - "WP2750: Development of Solvent-Free Nitration Processes Using *tert*-Butyl Nitrite" Boruta, D. T. IHTR 3742, 2018.

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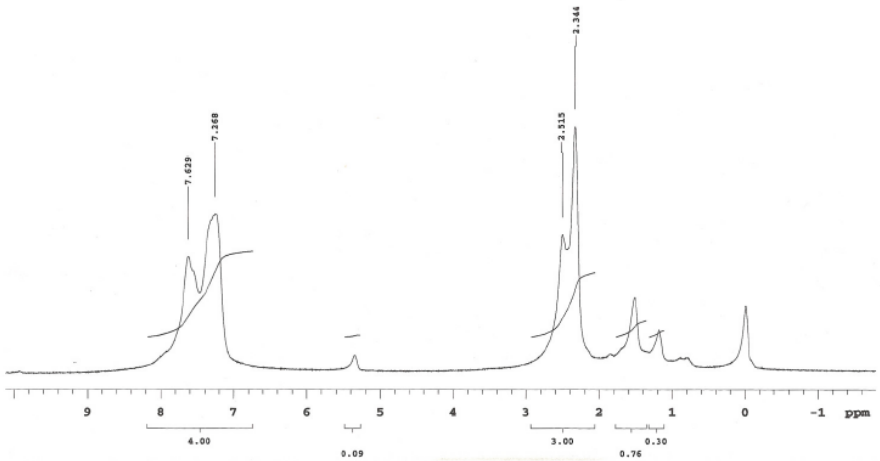
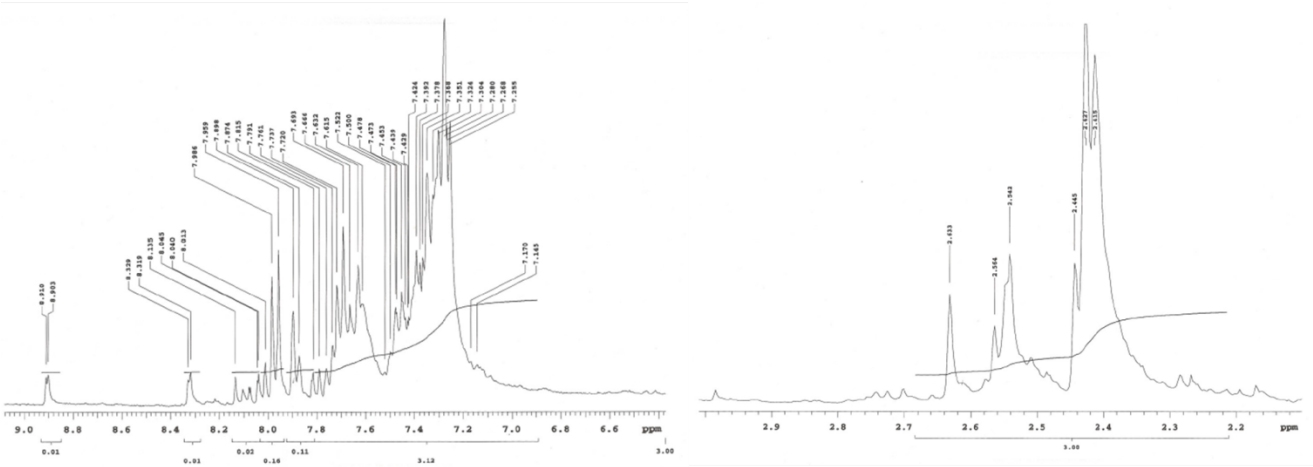
BACKUP SLIDES

NMR Data – Toluene Nitration



^{1}H NMR Spectra of Chromatographed Mono-nitration Isomeric Mixture; Contains Complexed Copper which is Causing Peak Broadening in the Spectral Data



^{1}H NMR Spectra (magnified) of Chromatographed Di-nitration Isomeric Mixture

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WP-2750: Development of Solventless Nitration Processes Using tert-Butyl Nitrite

Performers:

- PI: Dr. David T. Boruta
- Analytics: Aaron S. Jenkins

Technology Focus

- Solventless nitration strategies that generate limited, but environmentally friendly waste streams.

Research Objectives

- Solventless nitration development using *tert*-butyl nitrite to access nitrate esters, nitroarenes, and/or nitramines.

Project Progress and Results

- Investigated solventless nitrate ester synthesis from alcohols; only trace amounts of NG were formed. Nitrites were the major products.
- Investigated solventless nitration of toluene – was able to obtain isomeric mixtures of mono- and di-nitrotoluene in low yields through use of a copper catalyst.
- Investigated solventless nitrolysis of hexamine with companion nitrate salts; discovered reactivity was possible in trace amounts if small amounts of solvent was added.

Technology Transition

- This work has been documented for posterity:
  - "WP2750: Development of Solvent-Free Nitration Processes Using *tert*-Butyl Nitrite" Boruta, D. T. IHTR 3742, 2018.
  - Boruta, D.T.; Jenkins, A. S. "Development of Solventless Nitration Processes Using *tert*-Butyl Nitrite," *Proceedings of the JANNAF 45th SMBS/41st PEDCS/30th SEPS/PIB Joint Subcommittee Meeting,* Vancouver, WA, 2018.