

DIFLUORAMINO ENERGETIC MATERIALS

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Report Documentation Page

Form Approved
OMB No. 0704-0188

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1. REPORT DATE APR 1995		2. REPORT TYPE		3. DATES COVERED 00-00-1995 to 00-00-1995	
4. TITLE AND SUBTITLE Difluoramino Energetic Materials				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) TPL Inc, An Advanced Materials Technology Company, 3768 Hawkins Street NE, Albuquerque, NM, 87109				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES 33	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

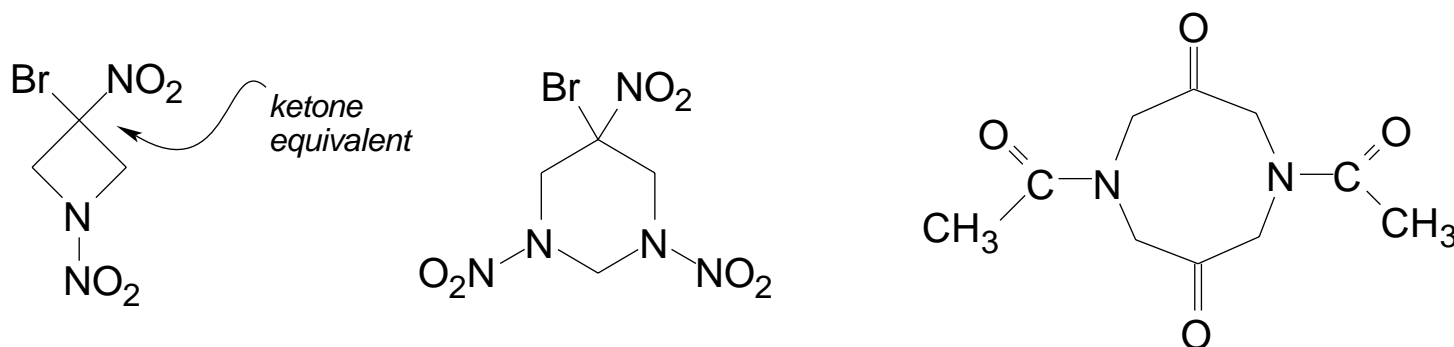
Difluoramino Nitramines

- The concept: Archibald & Baum (Fluorochem, 1988)
- NF_2 derivatives \rightarrow higher energy \rightarrow improved performance
- Mix of NF_2 and NO_2 to maintain insensitivity

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Community Meeting (China Lake, 1989)

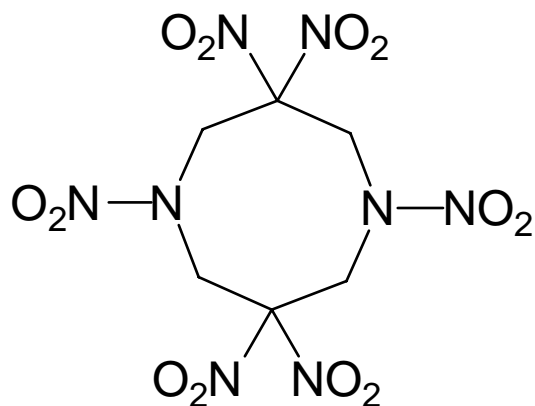
- Latest property predictions presented
- Intermediates toward target compounds first presented



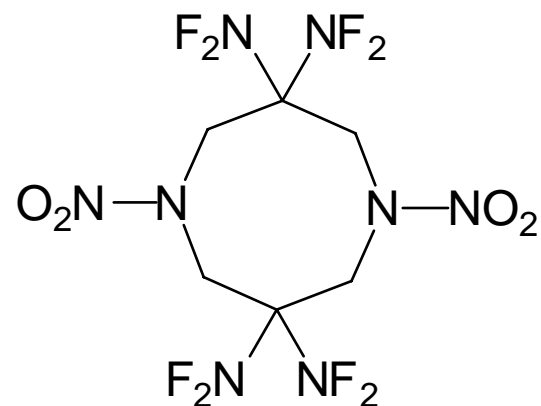
(Chapman, Fluorochem)

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Tetrakis(difluoramino)octahydro-1,5-dinitro-1,5-diazocine (TEDDZ)



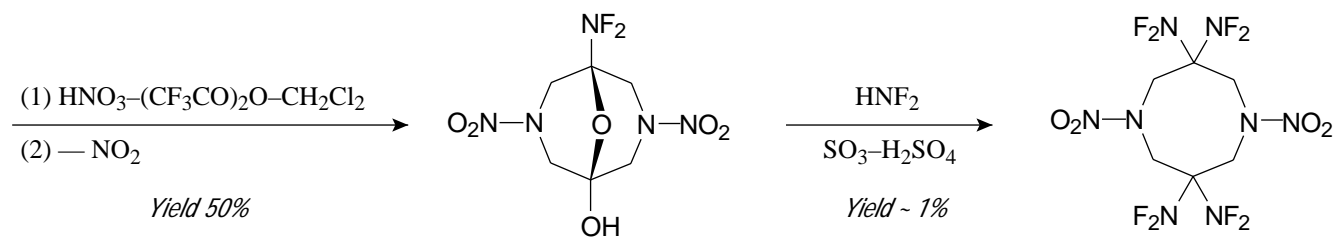
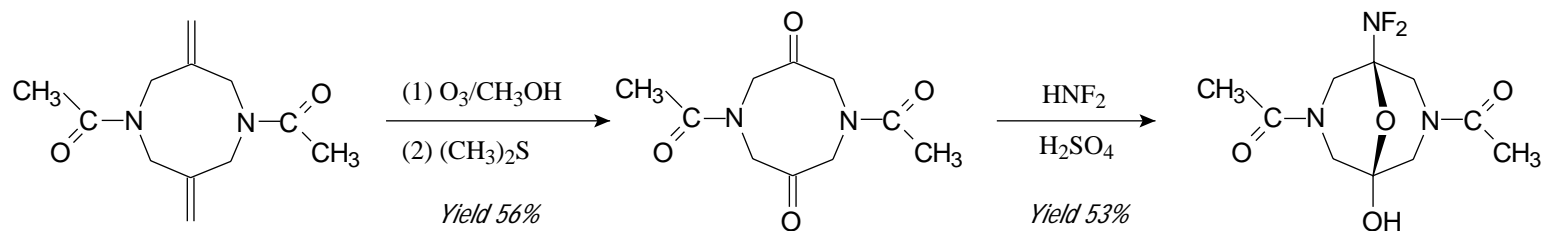
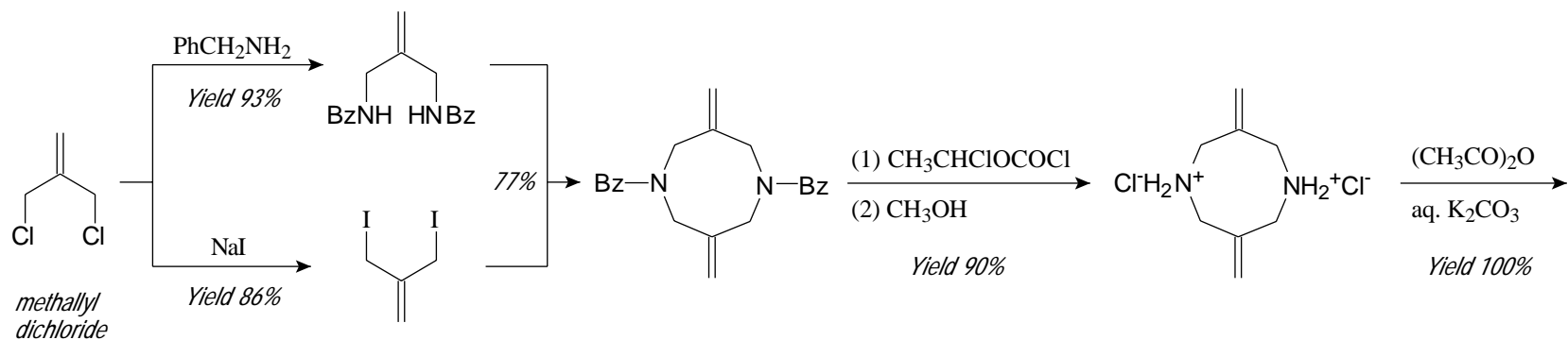
“HNDZ”
T.B. Brill *et al.*
J. Phys. Chem.
1985, 89, 4317



“TEDDZ”
or
“Teddy-Z”
“NFX”
“That NF₂ Compound”
“That HMX Analogue”

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First Synthesis of TEDDZ



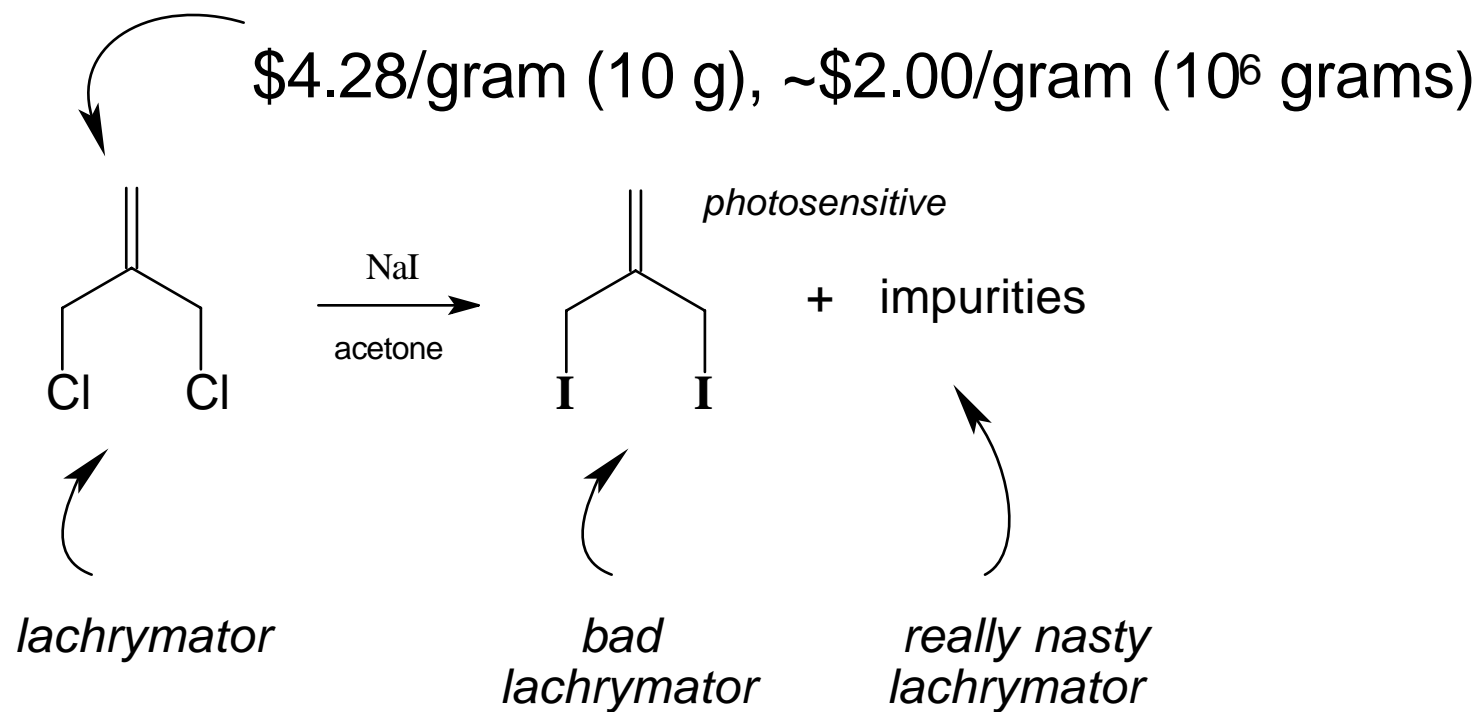
(Chapman, Fluorochem)

Original Route Drawbacks

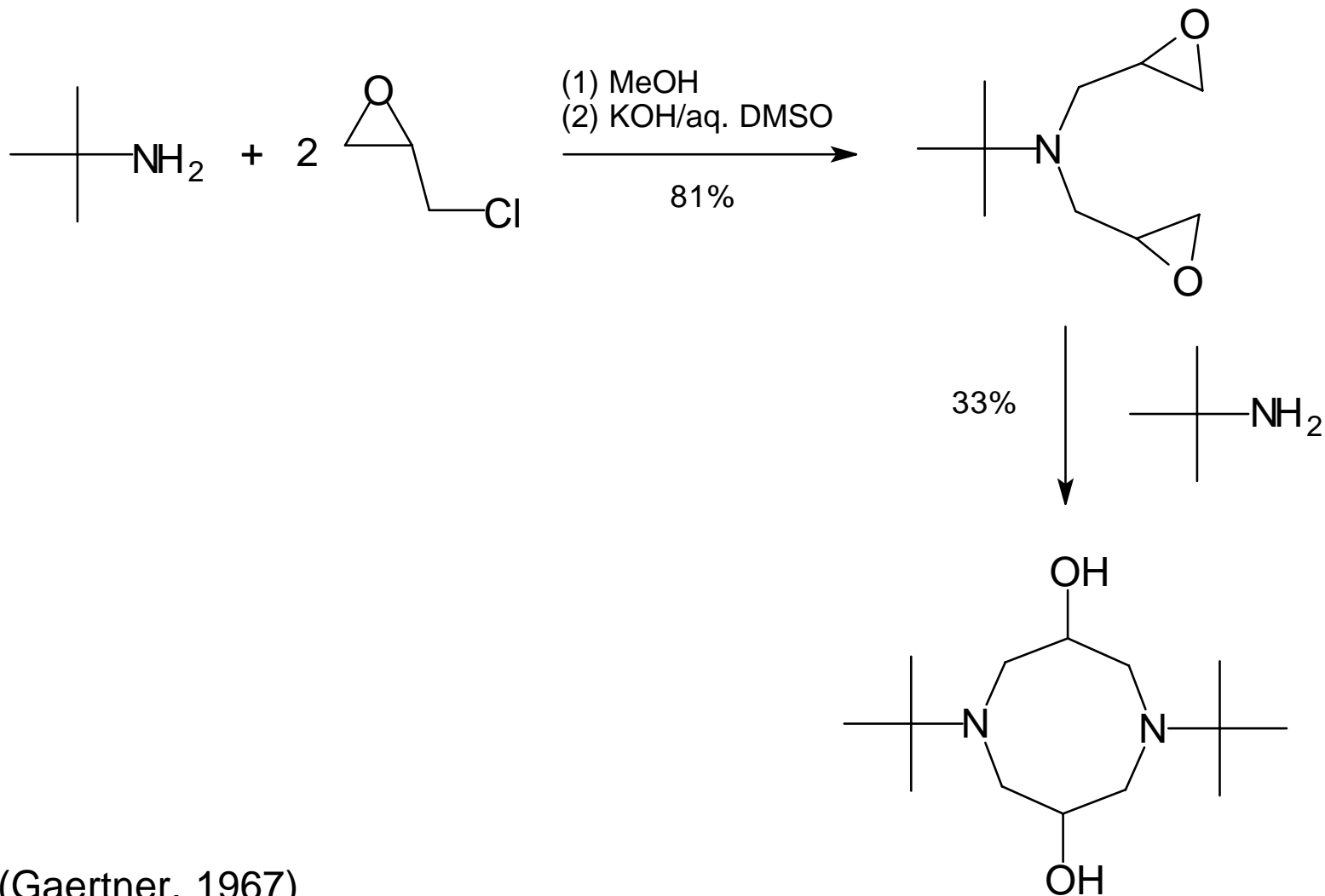
- Starting material
- Acetyl protecting group protonated under difluoramination conditions (\rightarrow deactivation) and unstable during prolonged reaction
- Nitramine “protecting group” unstable under difluoramination conditions \rightarrow terrible yield
- Difluoramine (HNF_2) treacherous

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Methallyl Dihalide Route



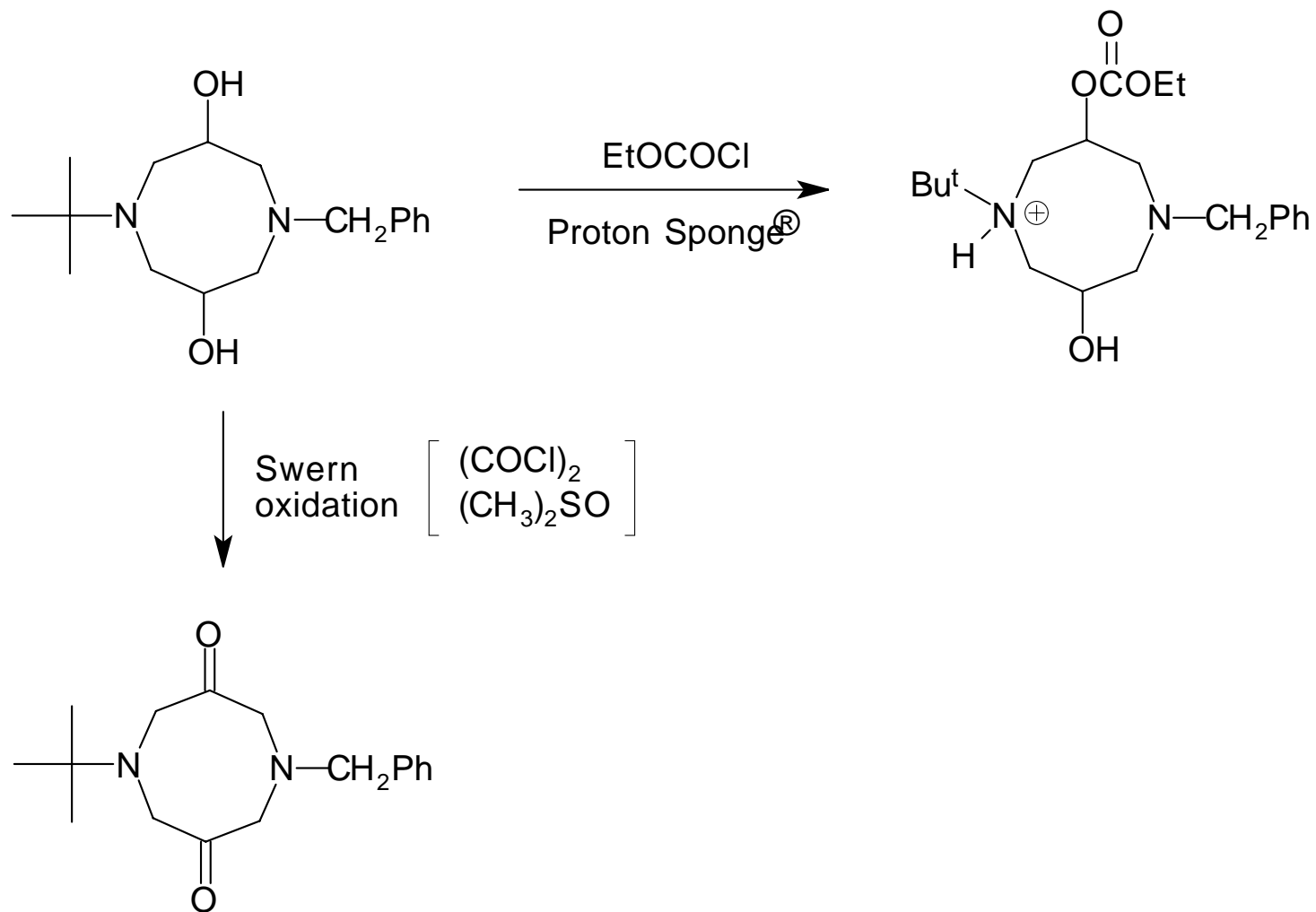
Alternative Diazocine Preparations



(Gaertner, 1967)

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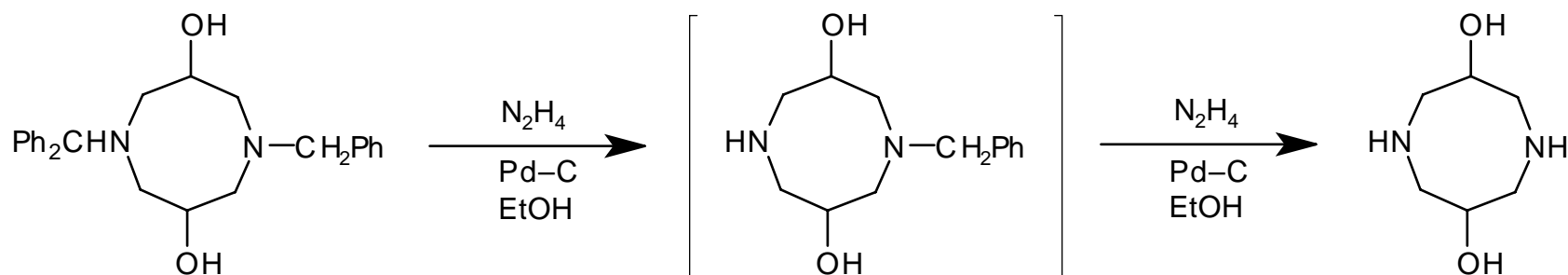
New Diazocine Derivatives



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New Diazocine Derivatives

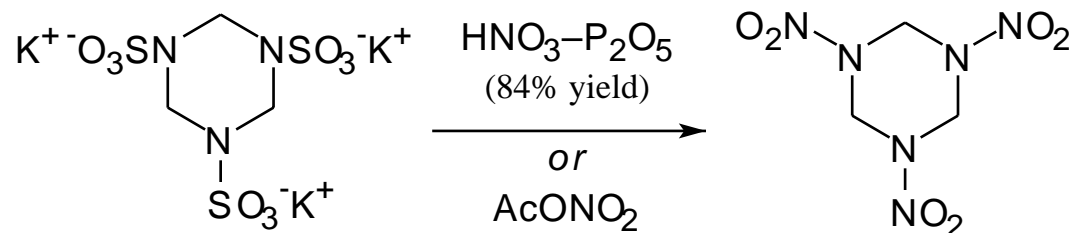
- *N*-Benzyl and *N*-benzhydryl easier to dealkylate than *t*-butyl



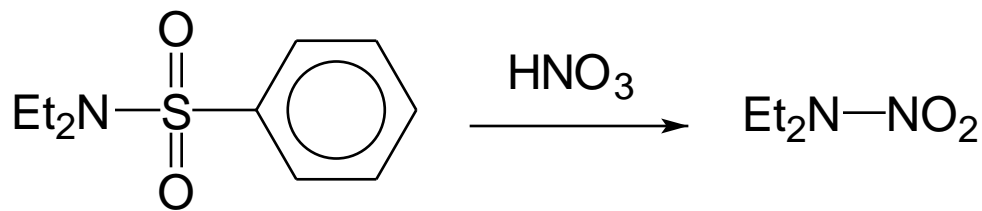
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Acid-Stable Nitrogen-Protecting Groups

- Sulfonic acid derivatives amenable to nitrolysis



(Wright, 1950)

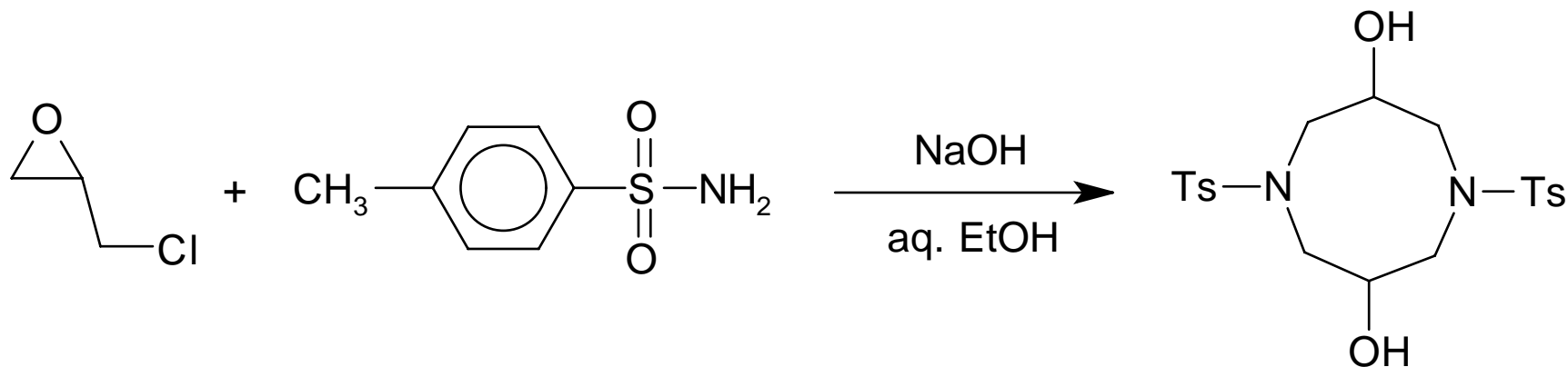


(van Romburgh, 1884)

- Sulfamic/sulfonic derivatives stable to sulfonating environment

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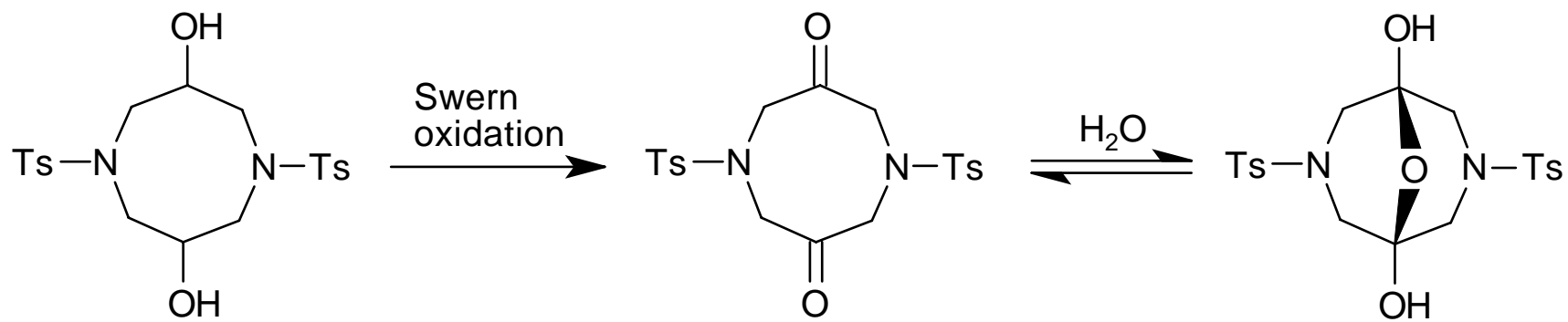
Alternative Diazocine Preparations



(Paudler & Zeiler, 1967)

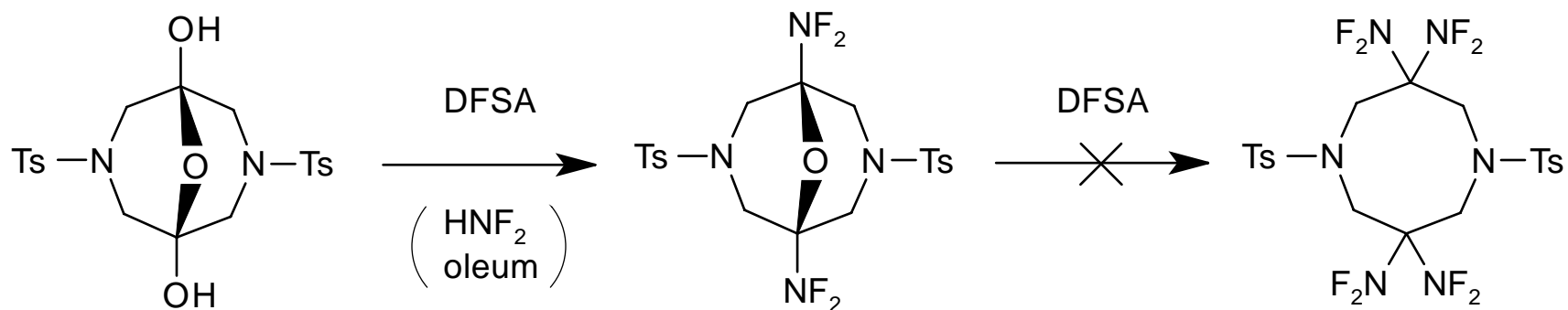
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Diazocinediones



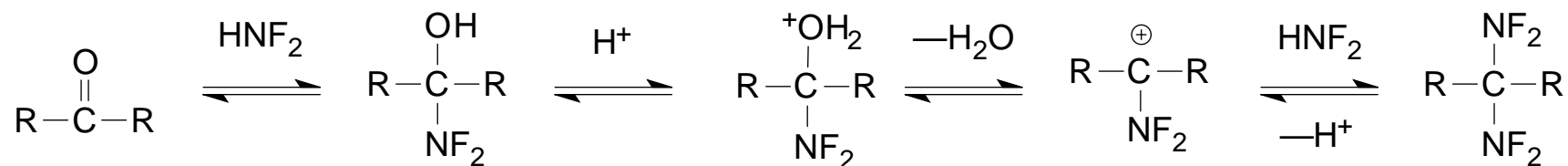
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Diazocinedione Difluoramination



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Difluoramination Mechanism

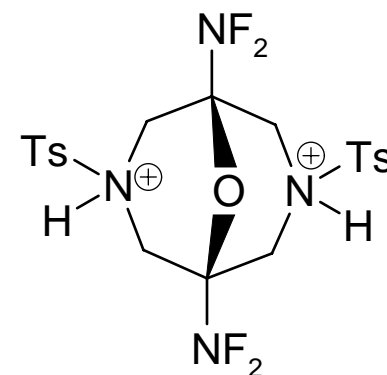
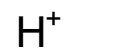
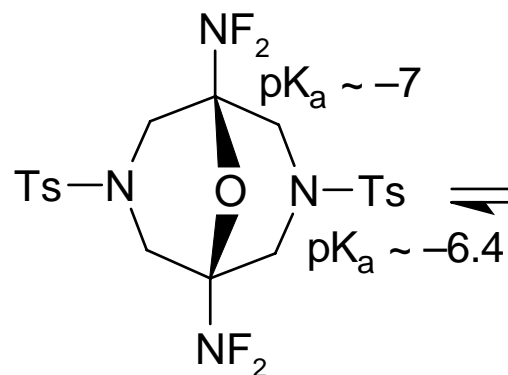
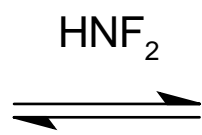
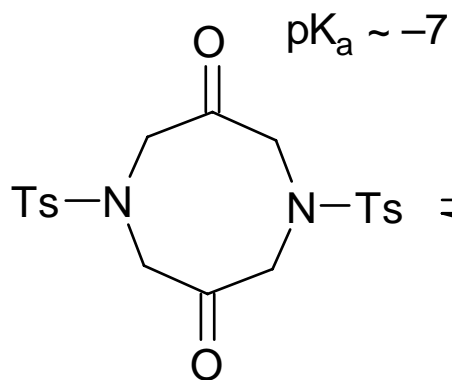
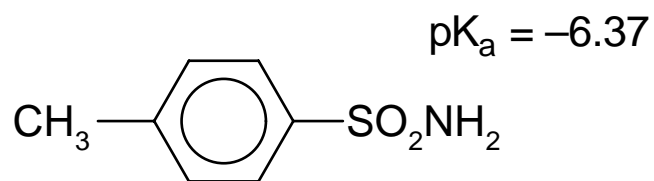
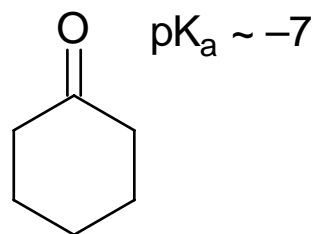


(Baum, 1968; Graham & Freeman, 1969)

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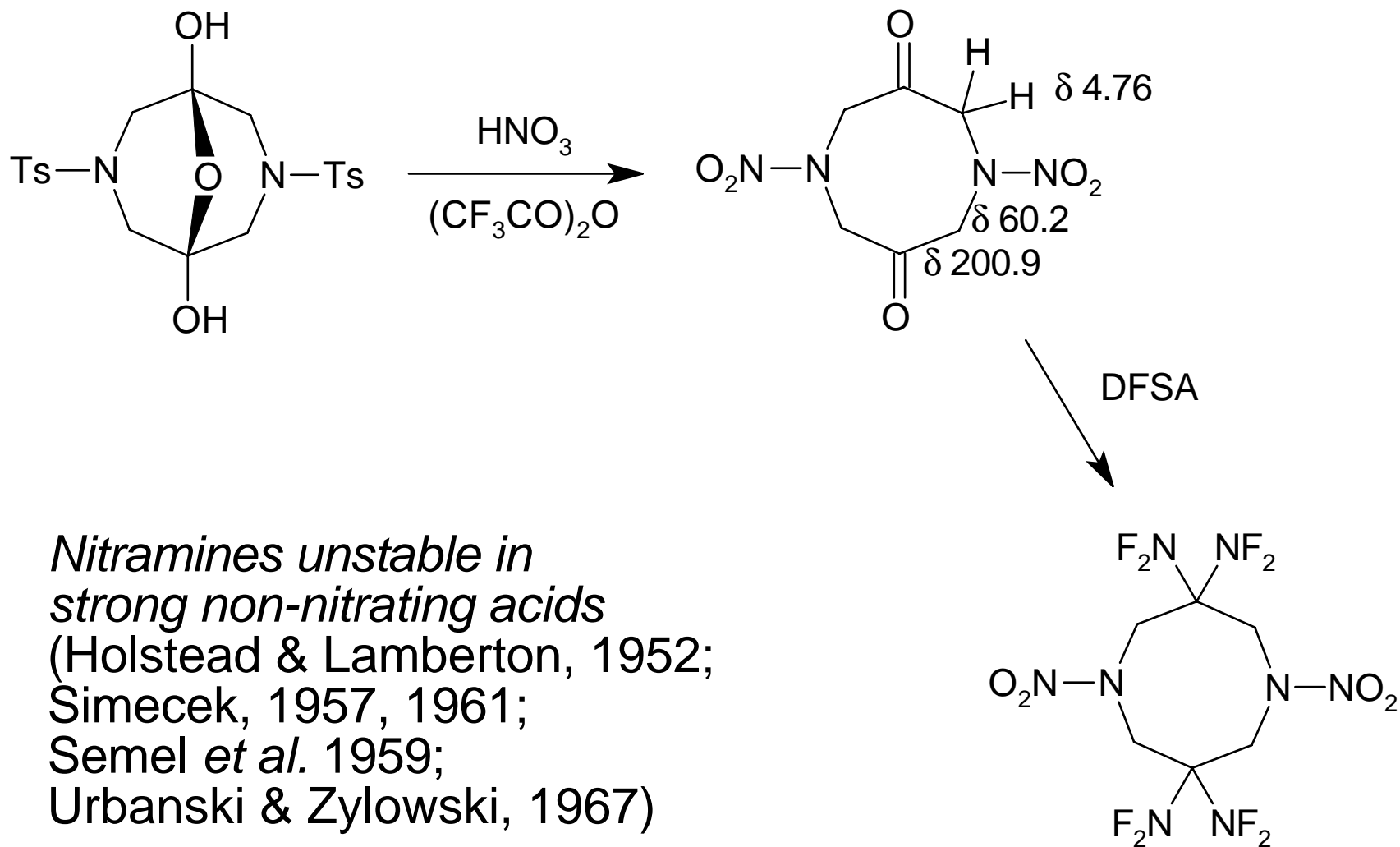
Difluoramination Dilemma

- Diazocinedione basicities



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Alternative Protecting Groups

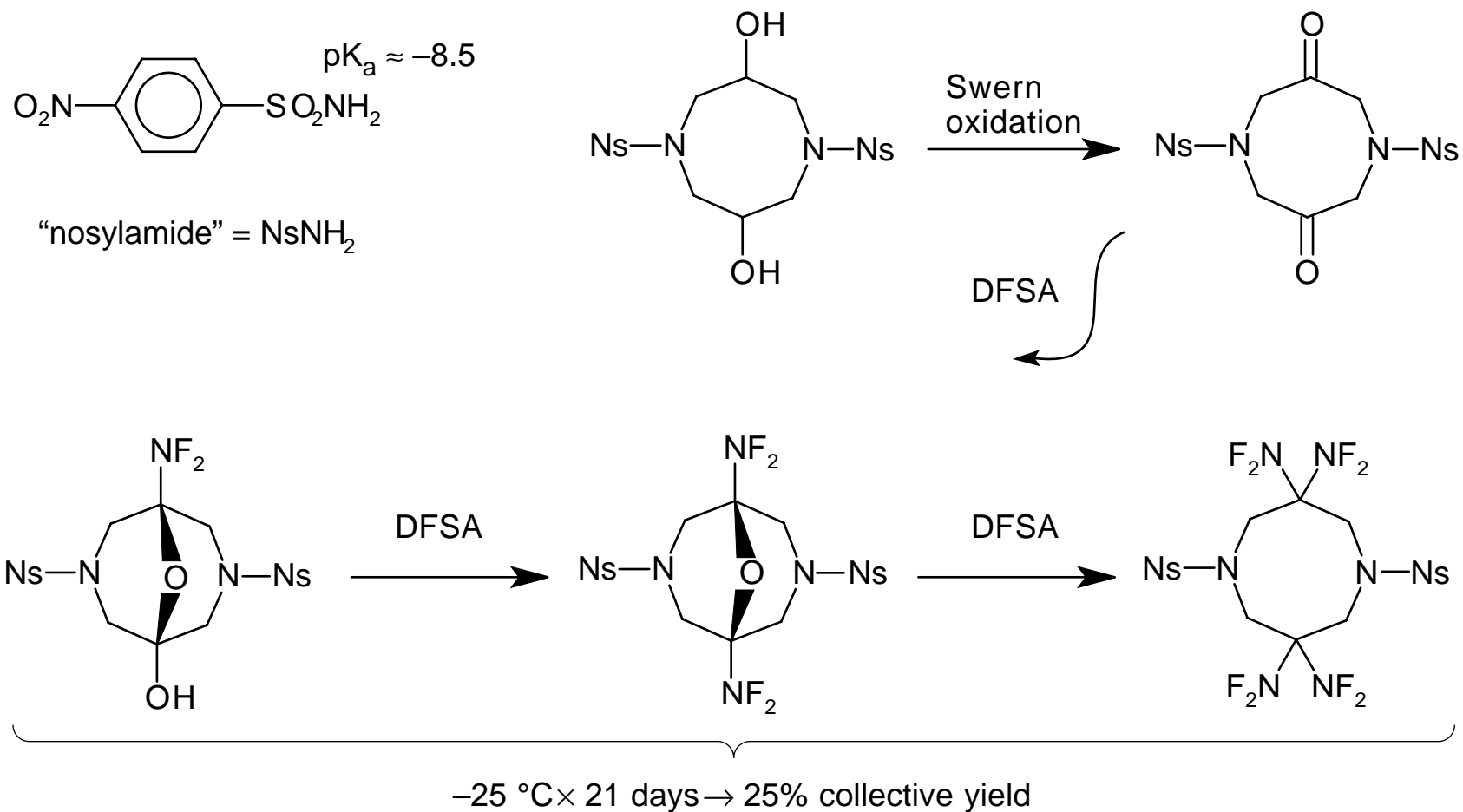


Nitramines unstable in strong non-nitrating acids
(Holstead & Lamberton, 1952;
Simecek, 1957, 1961;
Semel *et al.* 1959;
Urbanski & Zylowski, 1967)

~1% (many conditions)

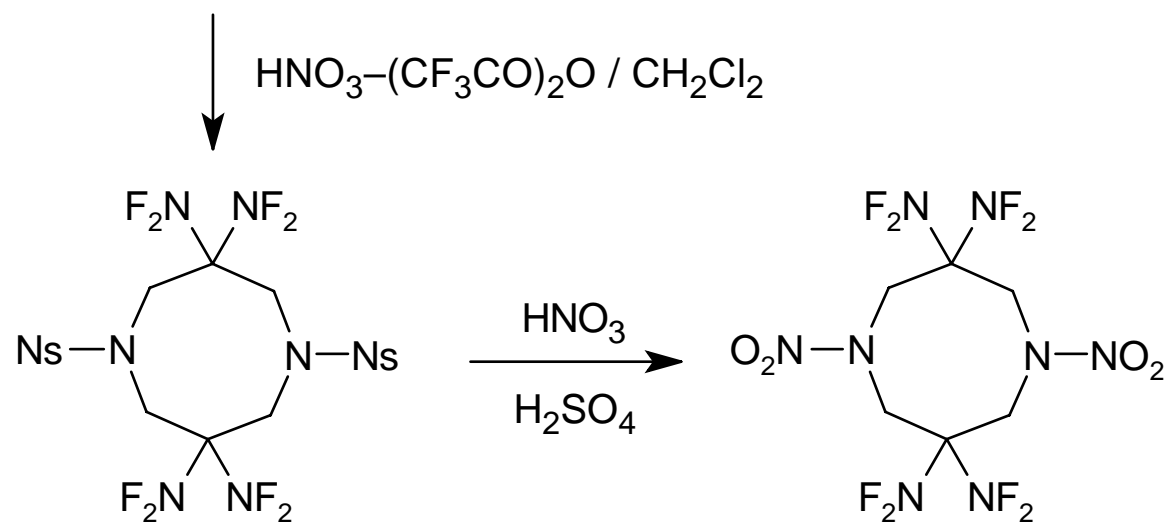
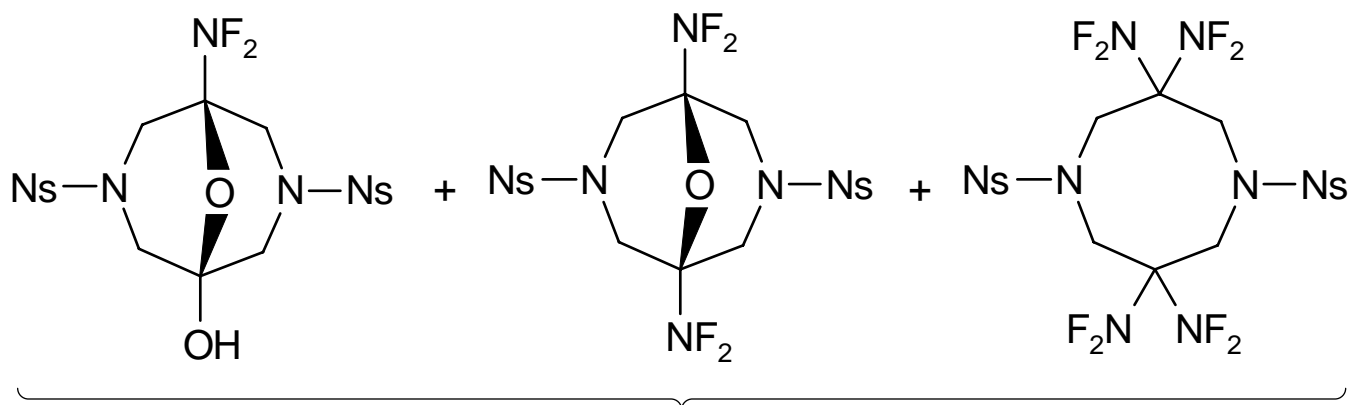
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Alternative Protecting Groups



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Nosyldiazocine Nitrolysis

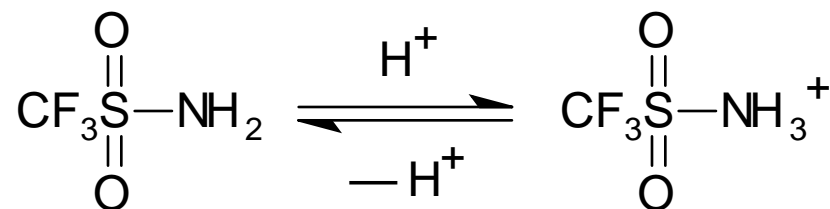


55 °C × 12 days →
100% conversion (clean);
70 °C × 6 days →
100% nitrolysis
(incl. 14% impurities);
90 °C × 2.5 hours →
44% conversion
(+ 16% impurities)

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Alternative Nitrogen-Protecting Groups

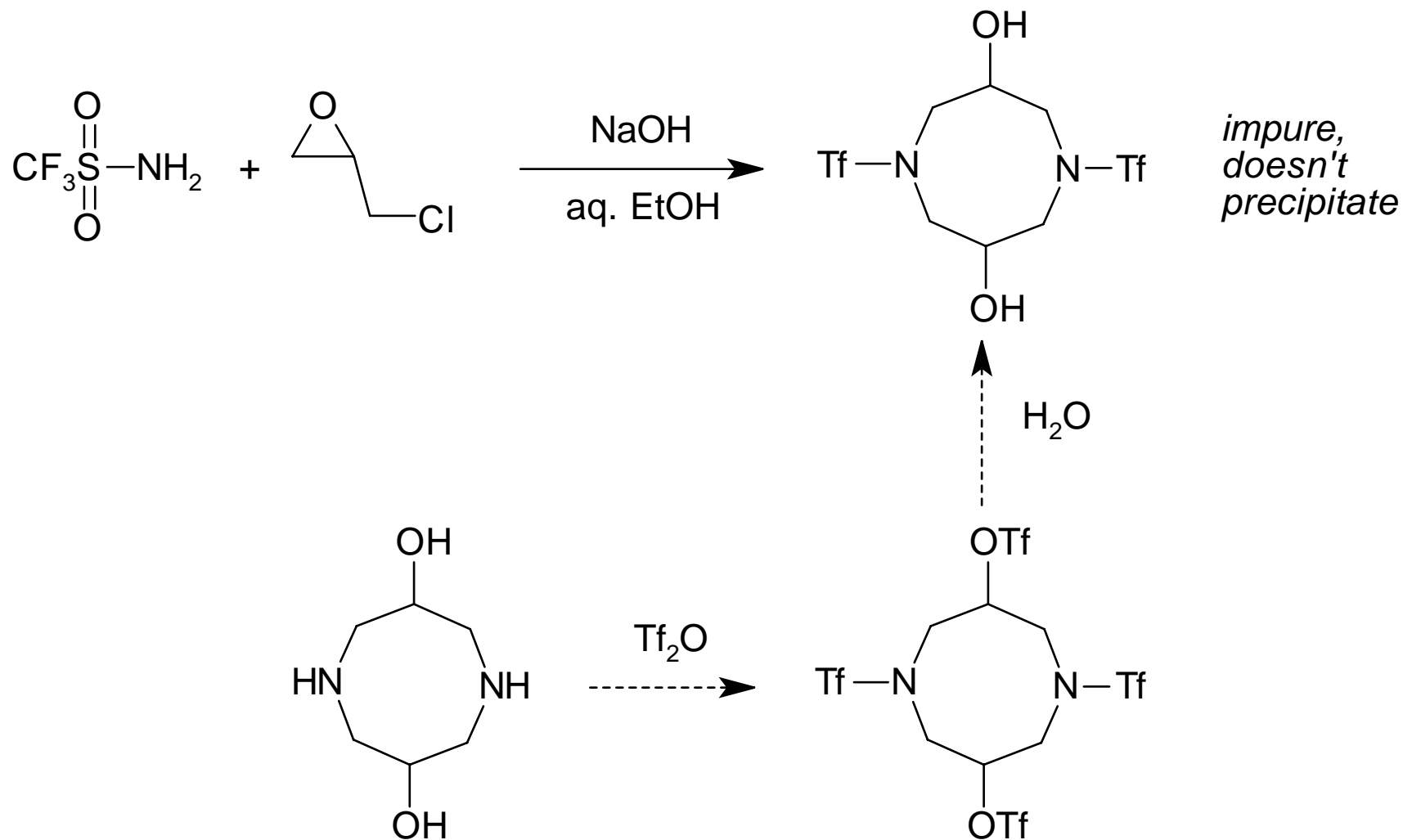
- Trifluoromethanesulfonamide basicity



<u>Solvent</u>	<u>H₀</u>	<u>¹⁹F NMR (δ)</u>	
CDCl ₃		-79.40	
D ₂ O		-79.95	
D ₂ SO ₄	-9.3	-78.99	
0.5% SO ₃ -H ₂ SO ₄	-11.1	-79.71 (57%) +	-75.86 (43%)
15% SO ₃ -H ₂ SO ₄	-12.8	-75.75	
15% SO ₃ -H ₂ SO ₄ + 20% D ₂ O		-78.97	
		pK _a ~ -11	

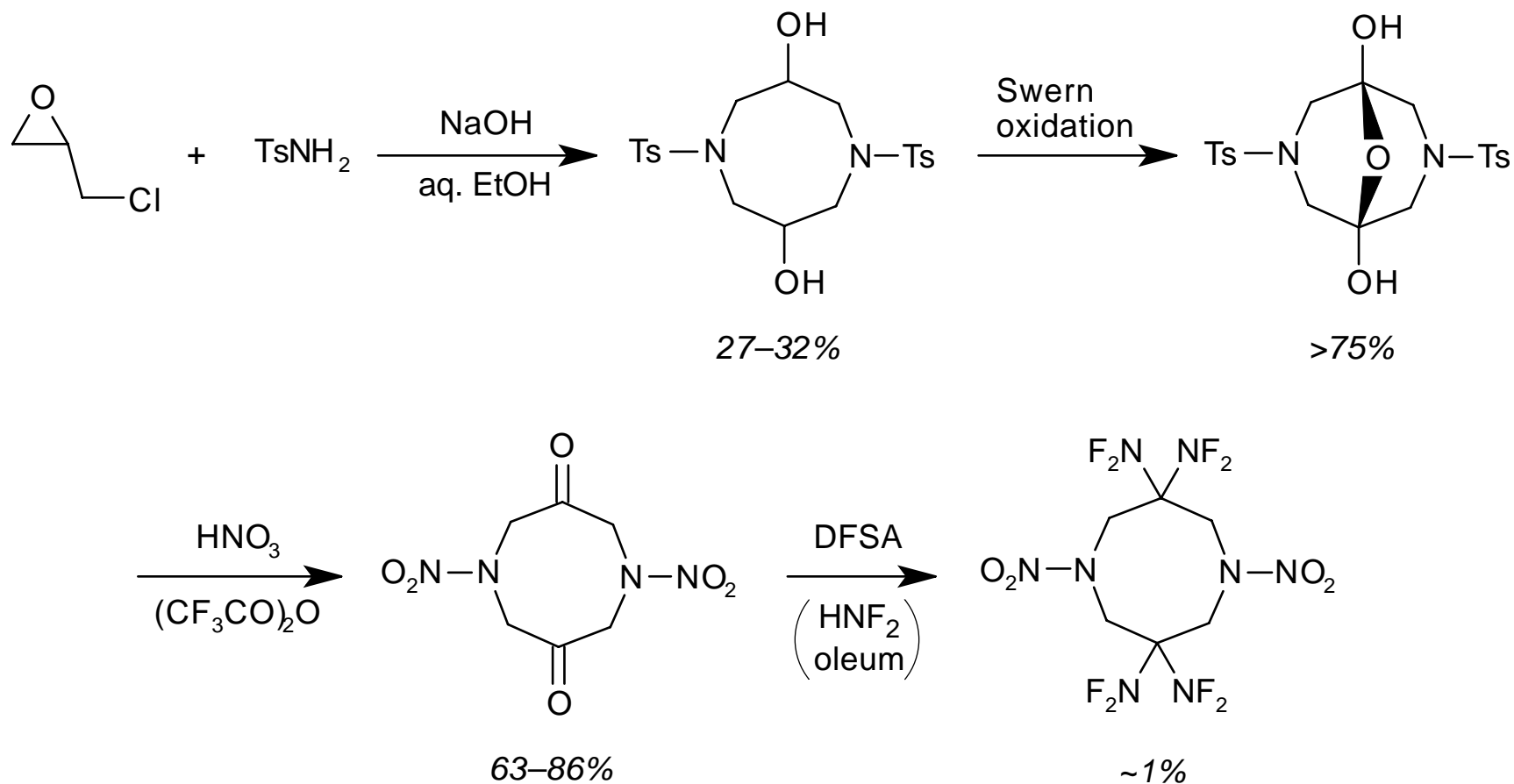
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Trifyldiazocines



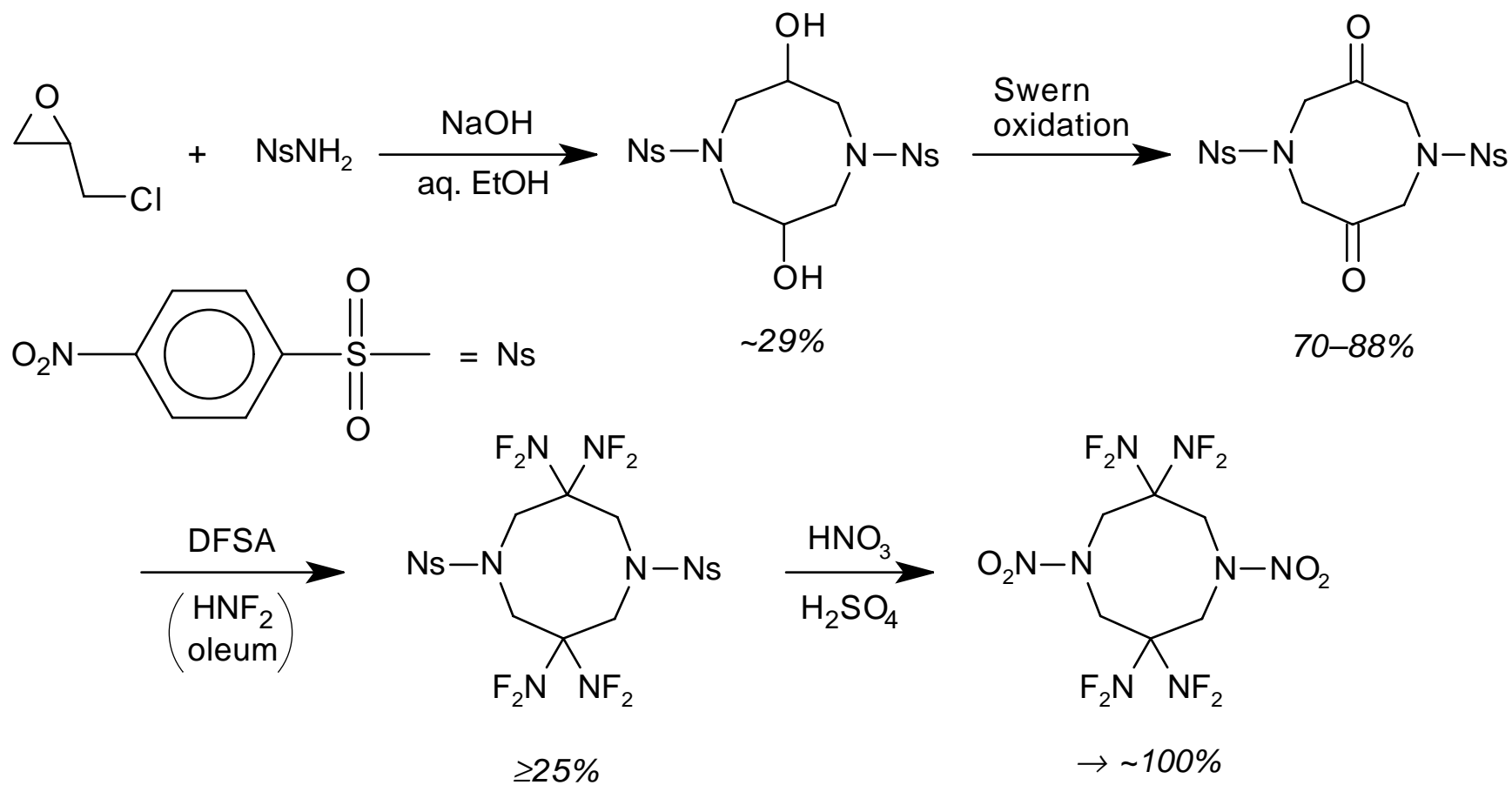
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The Best Demonstrated Route to TEDDZ



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The Best Apparent Route to TEDDZ



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TEDDZ Properties

- M.P. 202~203 °C(dec)
- Readily forms solvent adducts as HMX does
- Crystal structure (solvate) by Richard Gilardi (NRL)
- TEDDZ·solvent ρ 1.784
- Comparison of solvent adduct densities:

α -HMX	ρ 1.838	← ← ←	$\Delta\rho \approx 0.25$
HMX·DMF	1.607		
HMX·NMP	1.570		

TEDDZ·solvent $\rho = 1.784$

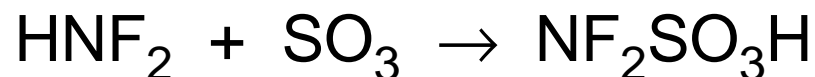
↓ $\Delta\rho \approx 0.25$

TEDDZ $\rho \approx 2.03$

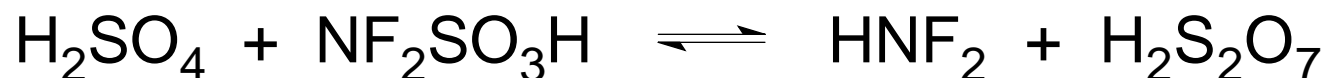
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Difluorosulfamic Acid (DFSA)

- $\text{NF}_2\text{SO}_3\text{H}$, a discrete species under typical difluoraminate conditions (Shoults/Rohm & Haas, 1967; Coon/SRI, 1973; Frankel *et al.*/Rocketdyne, 1979)



- Speculation about the nucleophilic species:

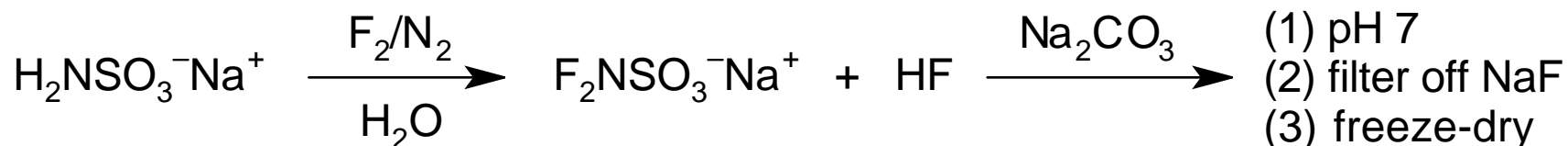


- DFSA is moderately stable in aqueous solutions (Archibald & Chapman, Fluorochem, 1990; Allied Chemical, 1961)

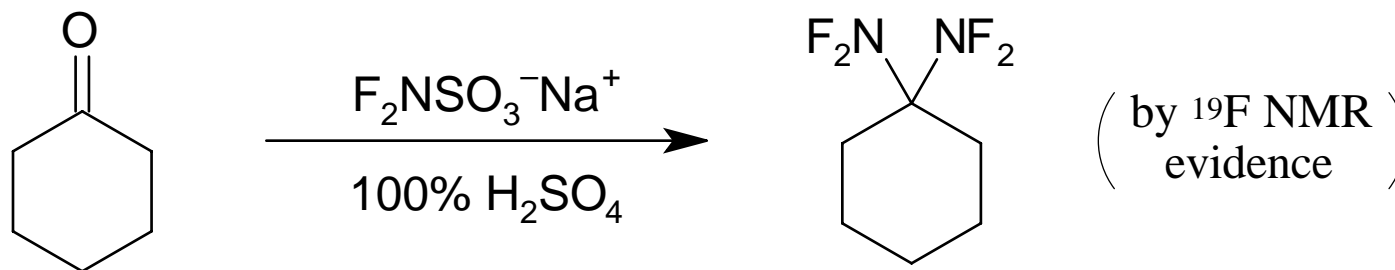
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Alternative Difluoramination Reagent

- Sodium difluorosulfamate (Na-DFSA)



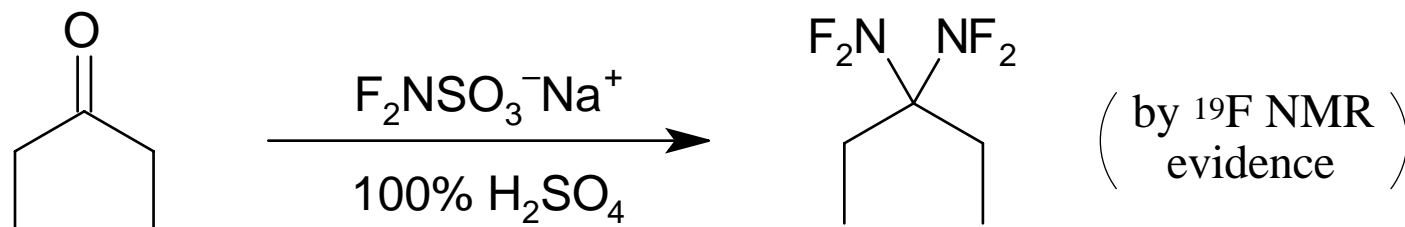
- Model difluoramination



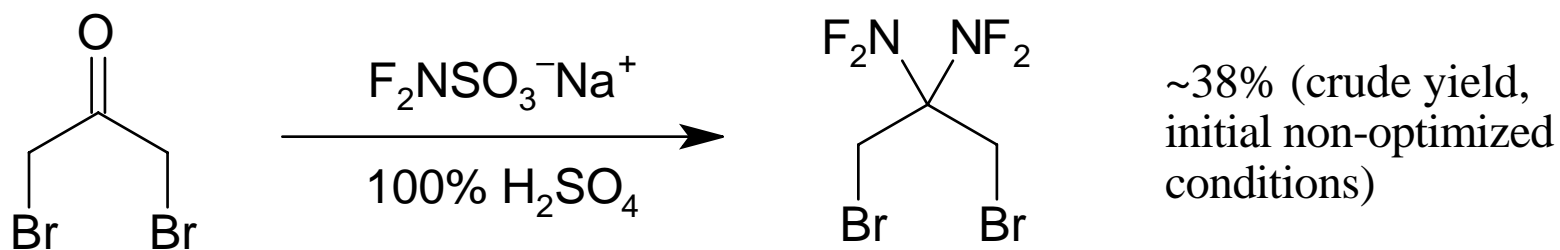
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Sodium Difluorosulfamate

- Another model difluoramination



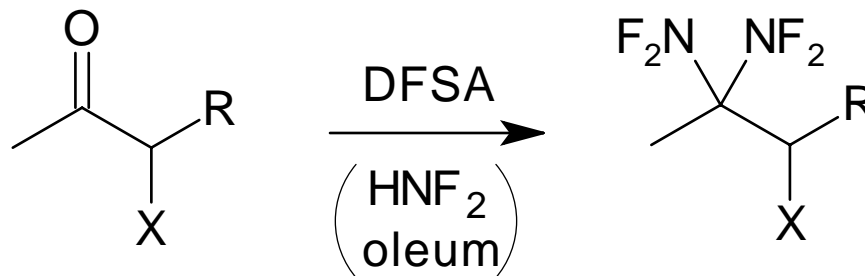
- A safe, convenient reagent of preparative utility!



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gem-Bis(difluoramino)alkyl Halides

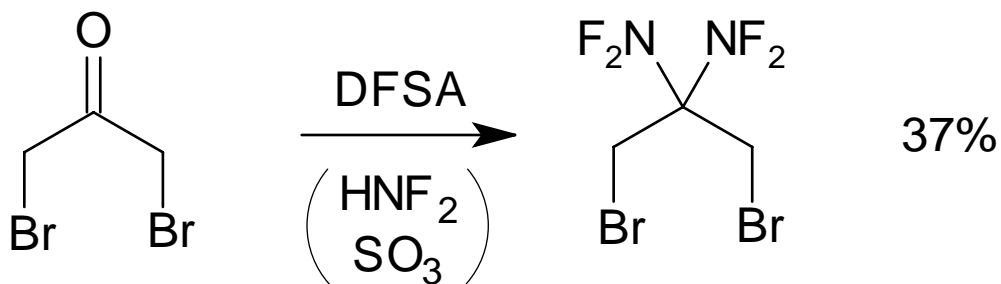
- α -Haloketone difluoraminations



X = Cl, R = H (Mitsch, 1968; Baum, 1968)

X = Br, R = H (Fokin, 1978)

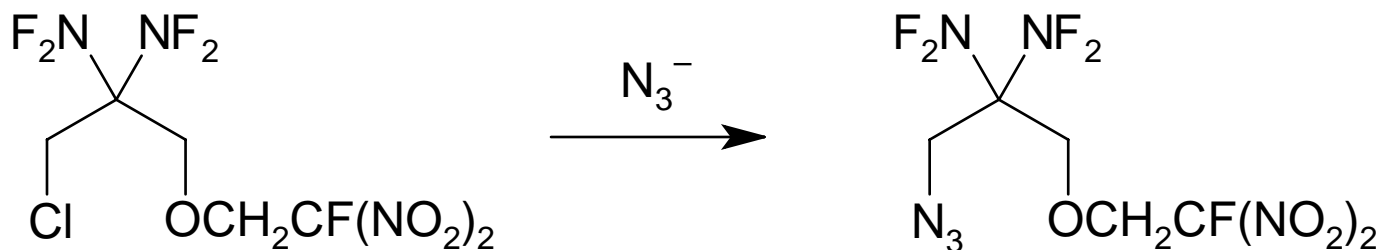
X = Br, R = CH_2Br (Orlando, 1971)



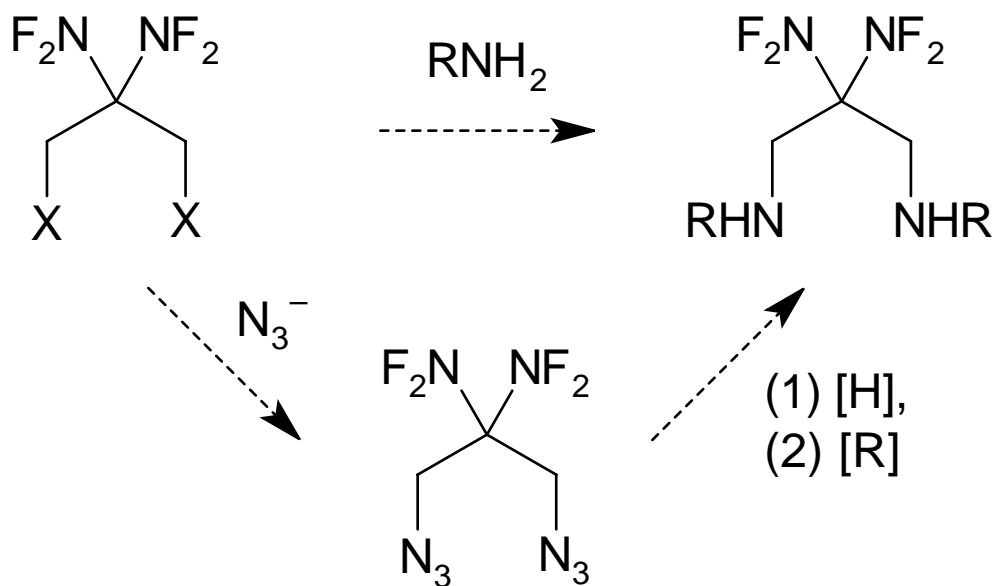
(Esso Research, 1962)

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gem-Bis(difluoramino) Diamines (Retrosynthetic)

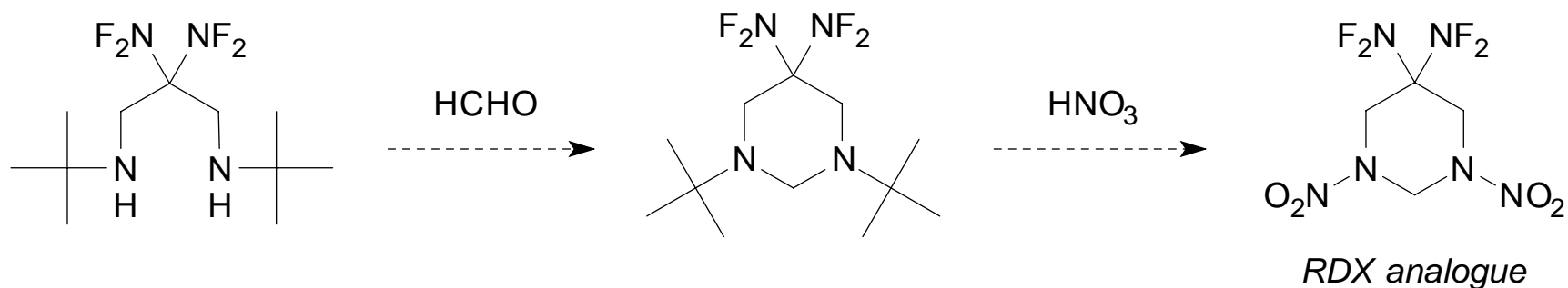
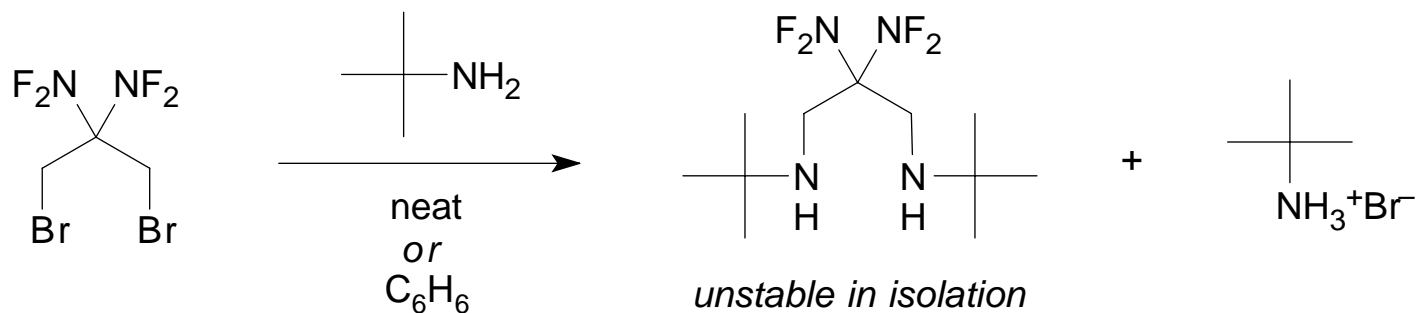


(Frankel & Witucki, 1982)



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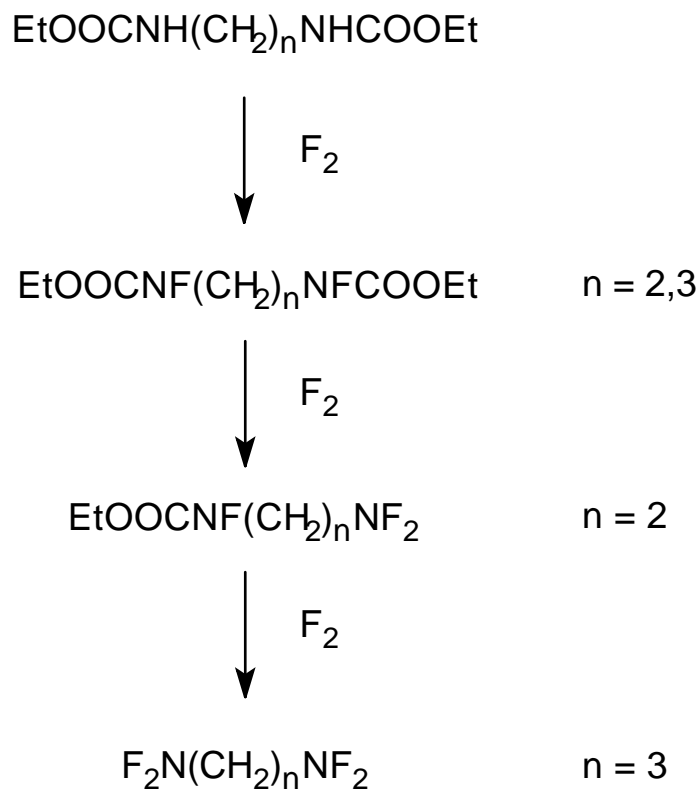
A *gem*-Bis(difluoramino) Diamine (Preliminary Result)



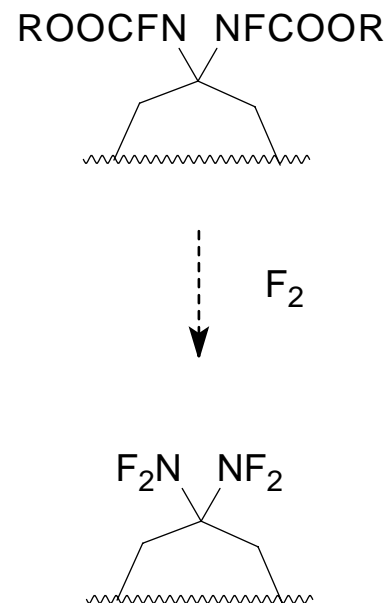
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Alternative Difluoramination Methodology (Proposed)

- Fluorination of *N*-fluorocarbamates



(Grakauskas & Baum, 1969)



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Conclusions

- *gem*-Bis(difluoramino)-substituted nitrogen heterocycles pose an inherently difficult synthesis
- TEDDZ offers great prospects but experimental complications
- Diazocinedione basicity is main obstacle
- Alternative routes to this system are being pursued
- Alternative difluoramination reagents are being pursued

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Acknowledgments

Funding

- Office of Naval Research (Dr. Richard Miller)
- Contract N00014-93-C-0126

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