LA-UR -87-1739

CONF-8705144--1

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36.

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LA-UR--87-1739

DE87 010129

SUBMITTED TO: Sixth Annual Working Group Meeting on Synthesis of High Energy Density Materials
Kiamesha Lake, NY
May 19-22, 1987

Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

FORM NO 836 R4

OXIDATION OF HETEROCYCLIC AMINES, SULFILIMINES, AND PHOSPHINE IMINES WITH DIMETHYLDIOXIRANE

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ABSTRACT

Our previous work[1] has shown that oxidation of 3-amino-4-(4-chlorophenyl)furazan (1) with peroxytrifluoroacetic acid (ptfa) gave azoxy (4-chlorophenylfurazan) (6) as the major product along with a small amount of 3-(4-chlorophenyl)-4-nitrofurazan (5). The dimethylsulfilimine 2 derived from 1 gave near quantitative yields of 5 when subjected to oxidation with either ptfa or m-chloroperoxybenzoic acid (mcpba). In contrast, both the trioctylphosphine imine 3 and the triphenylphosphine imine 4 derived from 1 were oxidized by mcpba to give 6 as the exclusive product (Fig. 1).

It was recently reported that dimethyldioxirane (DMD), which is conveniently prepared by oxidation of acetone with persulfate[2], will convert certain aromatic amines to nitro compounds in high yield. In contrast to our results with peracids, DMD reacted with 1 to yield 5 as the exclusive product, but with 2 to give the sulfoximine (7) as the major product with only a small amount of 5. However, treatment of 3 with DMD gave 5 as the exclusive product (Fig. 1).

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[1]M. D. Coburn, J. Heterocyclic Chem. 23, 421 (1986).

[2]R. W. Murray and R. Jeyaraman, J. Org. Chem. 50, 2847 (1985).

3-Amino-4-nitrofurazan (8) failed to react with DMD and its sulfilimine (9) and phosphine imine (10) derivatives gave the oxidized species 11 and 12 (Fig. 2). We were surprised to find that 4,4'-diamino-3,3'-bifurazan (13) would not react with DMD, since it is readily oxidized to 4,4'-dinitro-3,3'-bifurazan with ptfa.[3]

2-Aminopyridine (14) was converted to its N-oxide (15) with DMD and its sulfilimine (16) and phosphine imine (17) derivatives were oxidized smoothly to 2-nitropyridine (18) with DMD (Fig. 3).

Both 2-aminopyrimidine (19) and 2-amino-5-nitropyrimidine (20) gave the N-oxides 21 and 22 when treated with DMD. The sulfilimine derivative of 20 (23) was converted with DMD to the sulfoximine (24). Although not isolated, 2-nitropyrimidine may have formed when the phosphine imine of 19 (25) was treated with DMD (Fig. 4).

Treatment of 2-aminopyrazine (26) with DMD produced the 1,4-dioxide (27). The phosphine imine derivative (28) was converted to a mixture of oxygenated products, possibly 29 and 30; however, the sulfilimine (31) was smoothly oxidized to 2-nitropyrazine (32) with DMD (Fig. 5).

Oxidation of 3,6-diamino-1,2,4,5-tetrazine (33) with DMD gave the 1,4-dioxide (34), which is predicted to have a crystal density of 1.95 g/cm^3 by J. R. Stine. Treatment of the disulfilimine (35) derived from 33 with mcpba gave what appears to be 3-(S,S-dimethylsulfilimino)-6-nitroso-1,2,4,5-tetrazine (36), which was subjected to oxidation by DMD. The structure of the product has not been rigorously established, but the structure of the oxygenated product (37) is consistent with elemental analyses and spectral data thus far obtained (Fig. 6).

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[3]M. D. Coburn, J. Heterocyclic Chem. 5, 83 (1968).

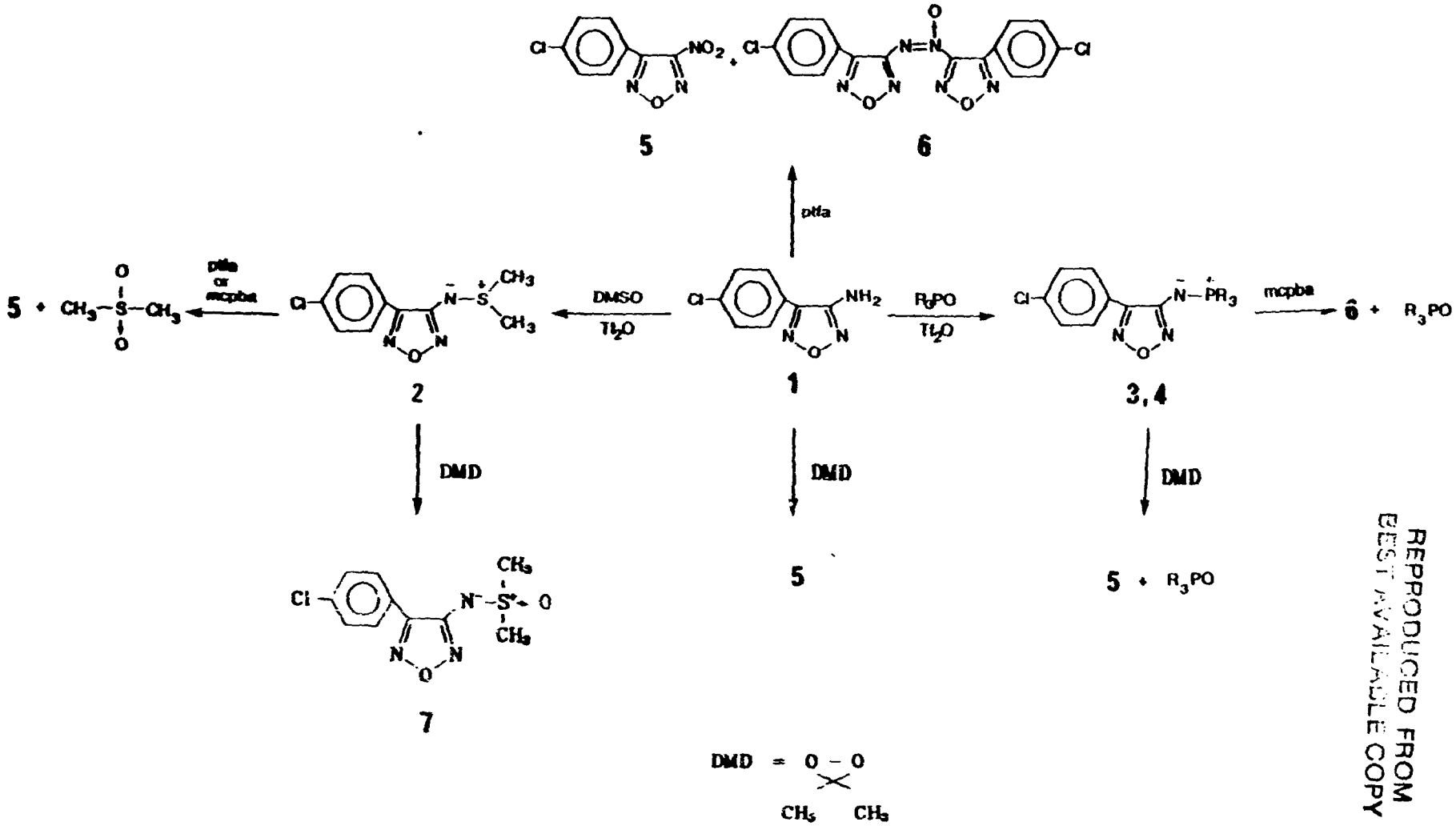


Figure 1. Oxidations of 3-amino-4-(4-chlorophenyl)furazan and its sulfilimine and phosphine imine.

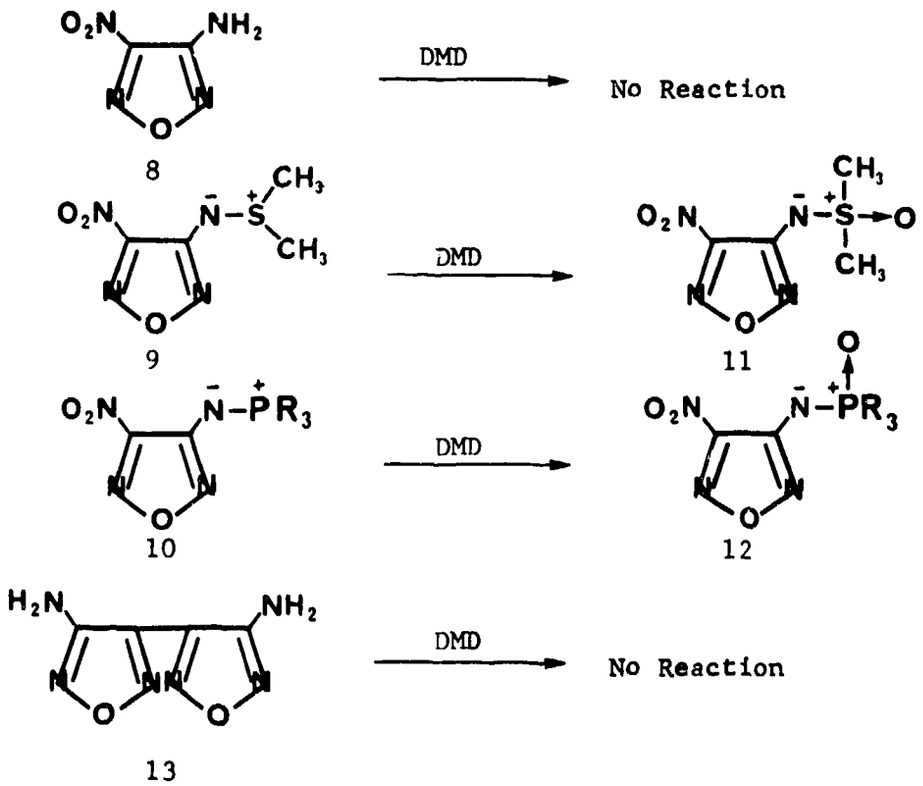


Figure 2. Oxidation of aminofurazans and their sulfilimines and phosphine imines with dimethyldioxirane.

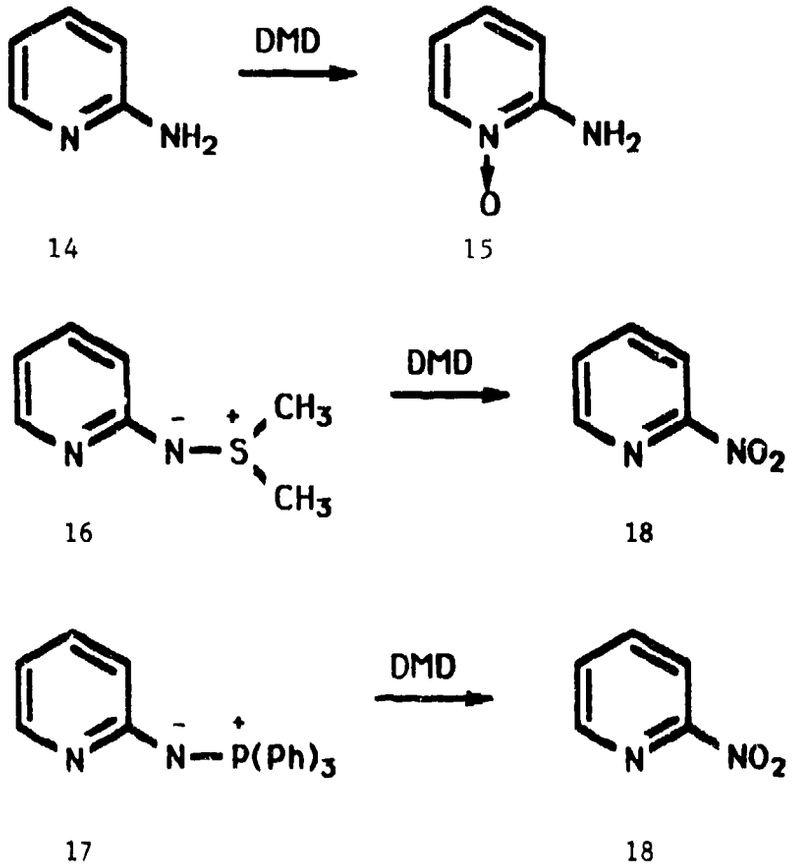


Figure 3. Oxidation of 2-aminopyridine and its sulfilimine and phosphine imine with dimethyldioxirane.

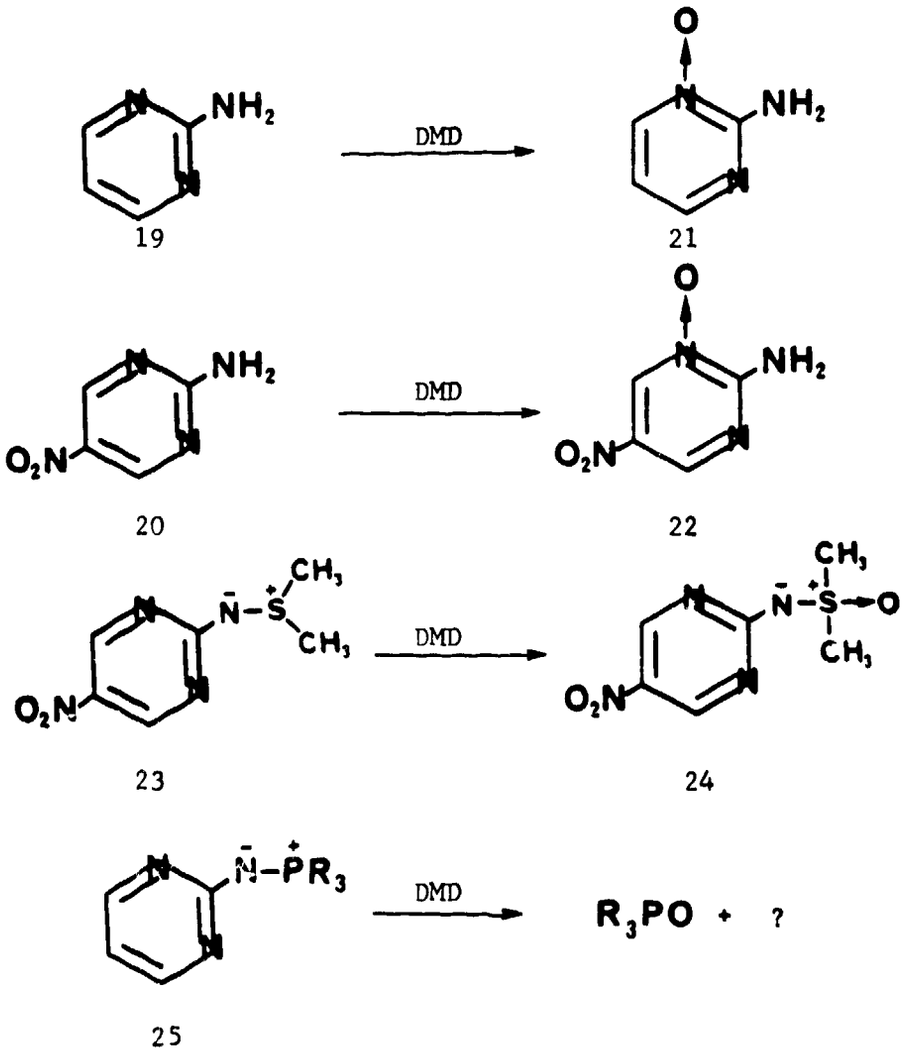


Figure 4. Oxidation of aminopyrimidines and their sulfilimines and phosphine imines with dimethyldioxirane.

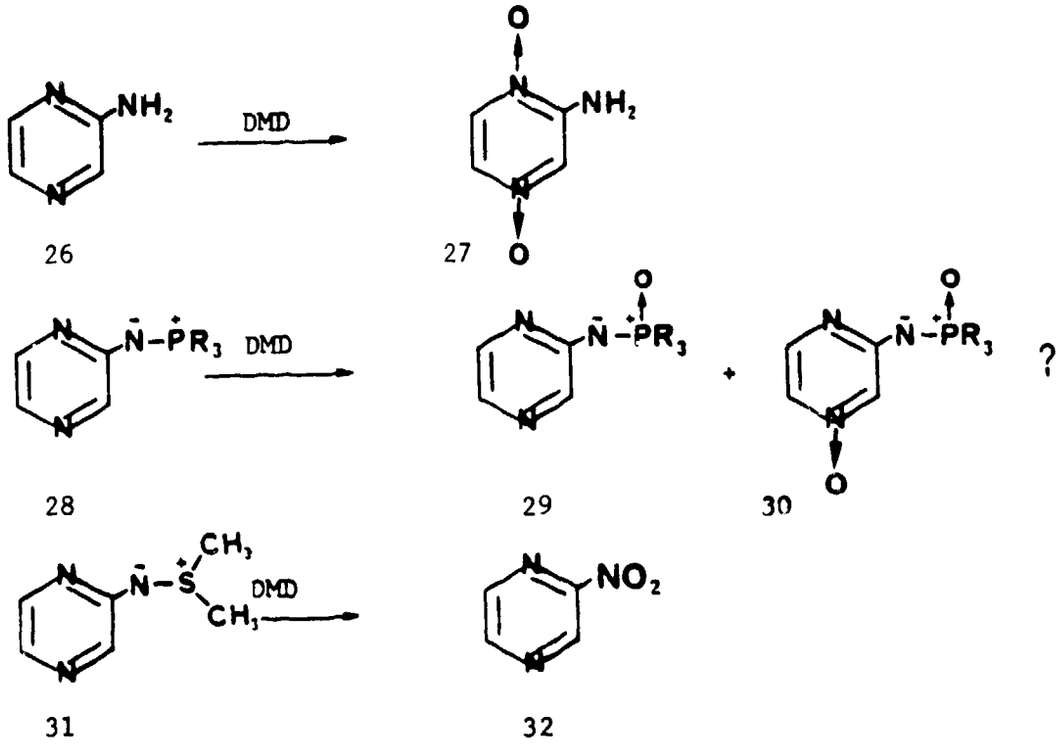
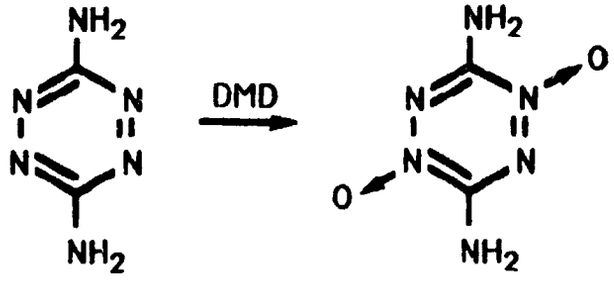
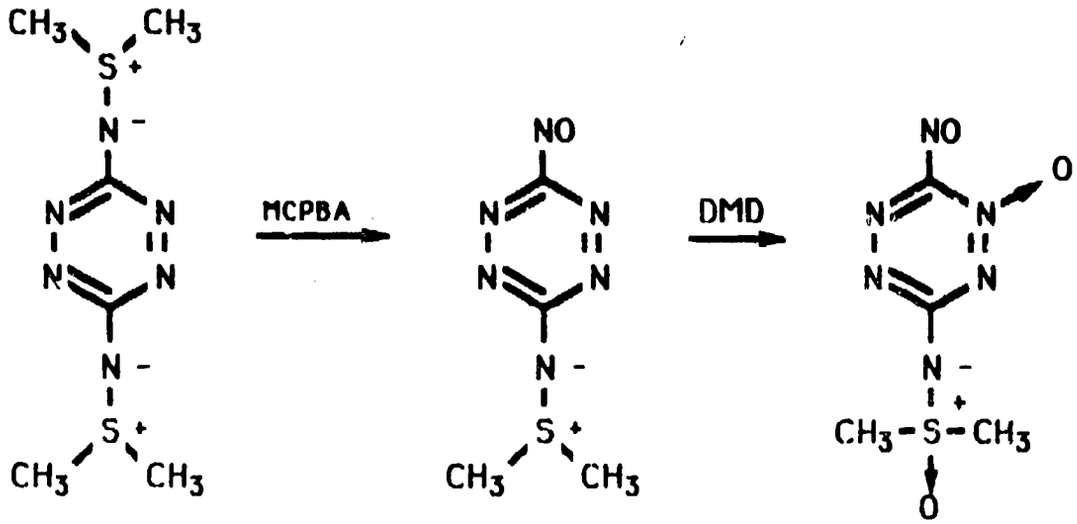


Figure 5. Oxidation of aminopyrazine and its sulfilimine and phosphine imine with dimethyldioxirane.



33 34



35 36 37

Figure 6. Oxidation of 3,6-diamino-1,2,4,5-tetrazine and its disulfilimino derivative.