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AUTHOR(S): Michael D. Coburn

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## Oxidation of Heterocyclic Nitrogen Ylids to Nitroheterocycles.

Michael D. Coburn

University of California, Los Alamos National Laboratory  
P.O. Box 1663, Los Alamos, NM 87545

In 1982, Taylor and coworkers reported the conversion of aminoheterocycles to nitroheterocycles by a two-stage oxidation of intermediate sulfiliminoheterocycles.<sup>1</sup> The sulfilimines were oxidized with *m*-chloroperoxybenzoic acid (mcpba) to the nitroso derivatives, which were treated with ozone to give the nitro compounds. The nitroheterocycles prepared by this method are 1-nitroisoquinoline, 2-nitropyridine, 2-nitropyrimidine, and 2-nitropyrazine. Hartman and Schwering subsequently employed this procedure to prepare some substituted nitropyrazines.<sup>2</sup> A more recent communication from Corey and coworkers describes the ozone oxidation of alkyl phosphine imines to nitroalkanes.<sup>3</sup>

Our interest in finding new routes to nitrofurazans led us to compare the oxidation of a sulfilimine and a phosphine imine derived from 3-amino-4-(4-chlorophenyl)furazan (1). The sulfilimine, 3-(4-chlorophenyl)-4-dimethylsulfiliminofurazan (2), was prepared by treating 1 with dimethyl sulfide ditriflate according to the procedure of Hartman and coworkers.<sup>4</sup> We discovered that the desired phosphine imine, 3-(4-chlorophenyl)-4-trioctylphosphiniminofurazan (3), could be prepared analogously by adding 1 to a solution of trioctylphosphine ditriflate, which was obtained by treating trioctylphosphine oxide with triflic anhydride (Tf<sub>2</sub>O) in dichloromethane. The corresponding triphenylphosphine imine (4) was also prepared by this new method, which is much cleaner and gives higher yields than other methods of preparing phosphine imines from amines.<sup>5</sup>

Oxidation of 1 with peroxytrifluoroacetic acid (ptfa) in dichloromethane gave a mixture that was chromatographed to give 3-(4-chlorophenyl)-4-nitrofurazan (5) in 11% yield and azoxy(4-chlorophenyl)furazan (6) in 32% yield. Under the same conditions, 2 gave a 96% yield of 5 with no trace of 6 (Fig. 1). Similar results were obtained when 2 was treated with mcpba. In contrast, 3 was recovered unchanged after treatment with ptfa, but was converted to 6 with no trace of 5 when treated with excess mcpba. In the latter reaction, optimum yields of 6 could be obtained when a ratio of mcpba to 3 of 1.5 was employed. When less peracid was used, some unreacted 3 was recovered along with 6, but the by-product in all cases was trioctylphosphine oxide, exclusive of trioctylphosphine. Both 2 and 3 were found to be resistant to ozonolysis at 0°C. Compound 4 gave essentially the same results as 3 when subjected to these oxidation conditions.

The formation of 6 during the oxidation of 1 with ptfa is easily explained by the reaction of the intermediate nitrosofurazan with its precursor, the hydroxylaminofurazan. However, the formation of 6 with no trace of 5 from the oxidation of 3 with mcpba suggests that the nitroso compound is not an intermediate in this reaction, but that a dimeric species may be formed before the nitrogen-phosphorous bonds are ruptured. The failure of 3 to react with ptfa may be the result of irreversible protonation of 3 with trifluoroacetic acid present in the oxidation medium.

The  $^{13}\text{C}$ -NMR spectrum of 5 contains a triplet corresponding to the nitro carbon and the  $^{14}\text{N}$ -NMR signal of the nitro nitrogen is a sharp singlet with a width at half-height of 17 Hz. Thus, it appears that the nitro  $^{14}\text{N}$  is coupled with the nitro  $^{13}\text{C}$  in the classical manner with very little quadrupolar coupling, as we reported for 4,4'-dinitro-3,3'-bifurazan-4,4'- $^{13}\text{C}$ .<sup>6</sup> This phenomenon allowed us to use  $^{14}\text{N}$ -NMR spectroscopy to detect the presence of small amounts of 5 in reaction mixtures.

Oxidation of diaminofurazan (7) with ptfa gives 3-amino-4-nitrofurazan (8),<sup>10</sup> which was converted to the sulfilimine (9). Treatment of 9 with anhydrous ptfa in dichloromethane gave a solution that contained dimethyl sulfone according to  $^{13}\text{C}$ -NMR analysis, but no nitrocarbon could be detected.

However, the  $^{14}\text{N}$ -NMR spectrum contained a very sharp singlet with a width at half-height of 19 Hz and a chemical shift almost identical to that of 5. Thus, it appears that we may have formed dinitrofurazan (10) in solution, but we have not been able to isolate it in pure form as yet (Fig. 2).

In addition, we have prepared a series of poly(dimethylsulfilimio) heterocycles as potential precursors to polynitroheterocycles (Fig. 3). Oxidation of 3,6-bis(dimethylsulfilimino)-1,2,4,5-tetrazine (11) with mcpba gave a good yield of 3-dimethylsulfilimino-6-nitroso-1,2,4,5-tetrazine (12). Hydrolysis of 12 gave 3-amino-6-nitroso-1,2,4,5-tetrazine (13), which rapidly polymerized to 14 (Fig. 4).

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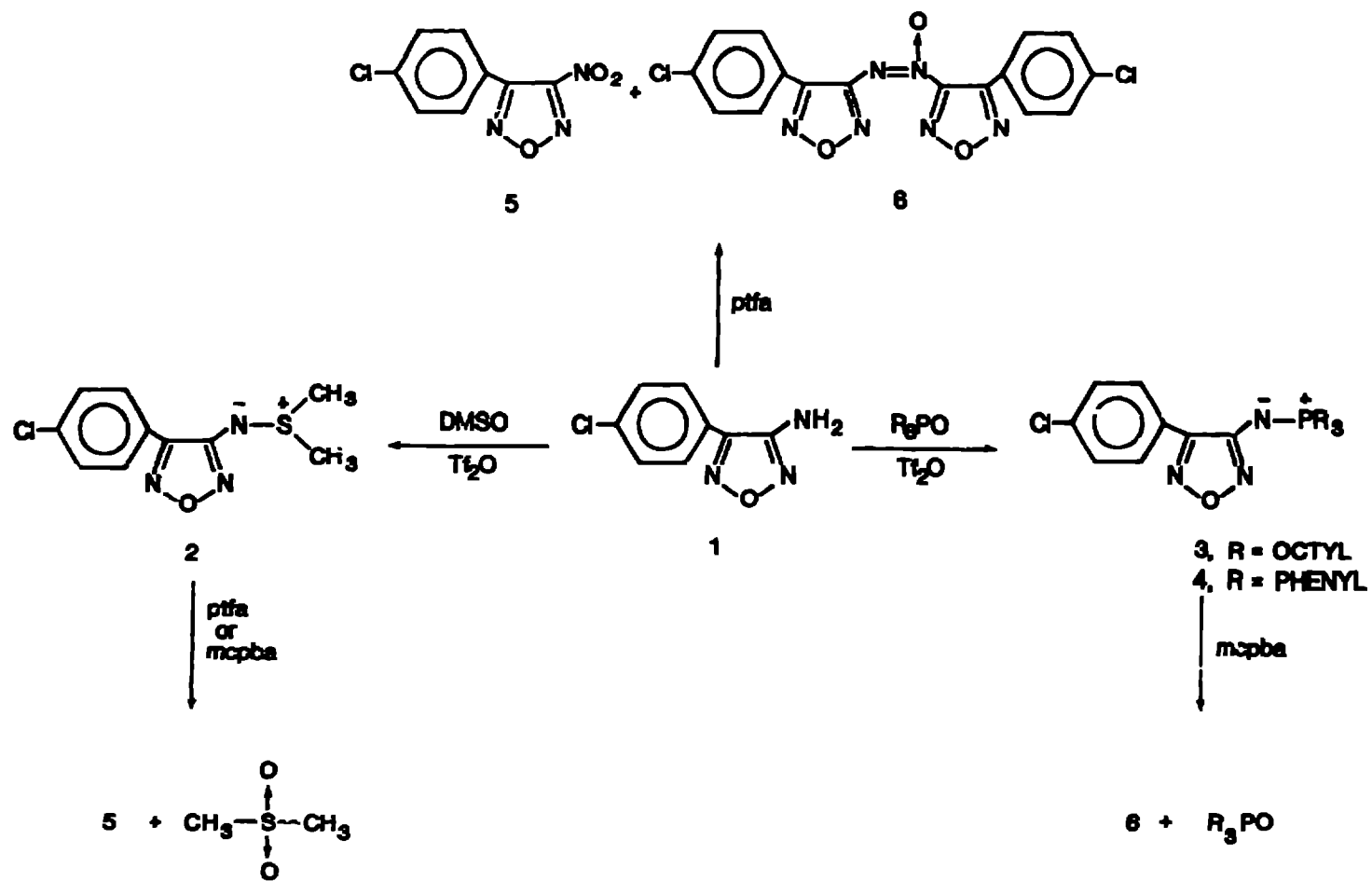


Fig. 1

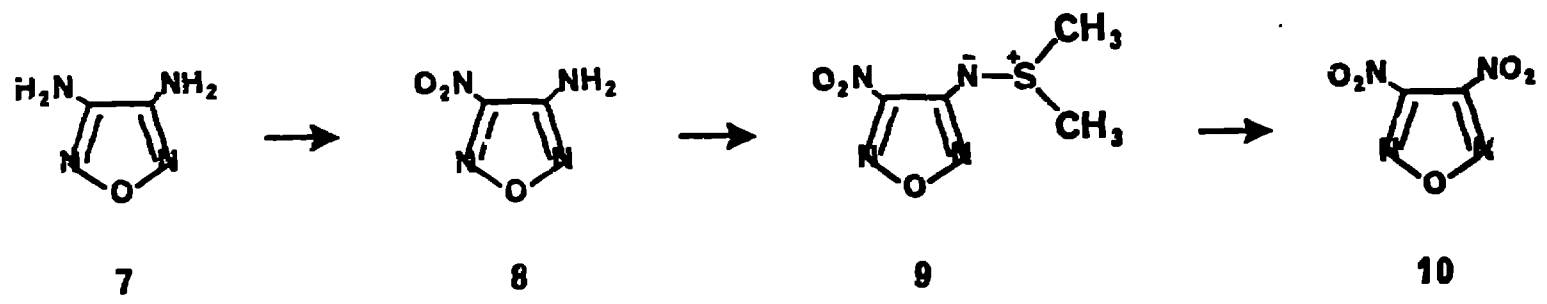
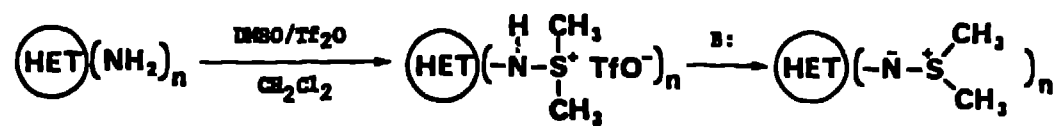


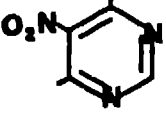
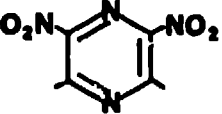
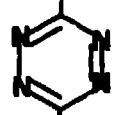

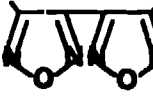

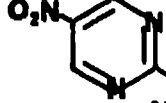

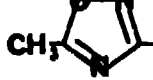


Fig. 2



	(HET)	n
a		3
b		2
c		2
d*		2
e		2
f		2
g		2
h*		2
i		1
j		1
k*		1

\*Prepared by C. L. Coon and A. R. Mitchell, Lawrence Livermore National Laboratory.

Fig. 3

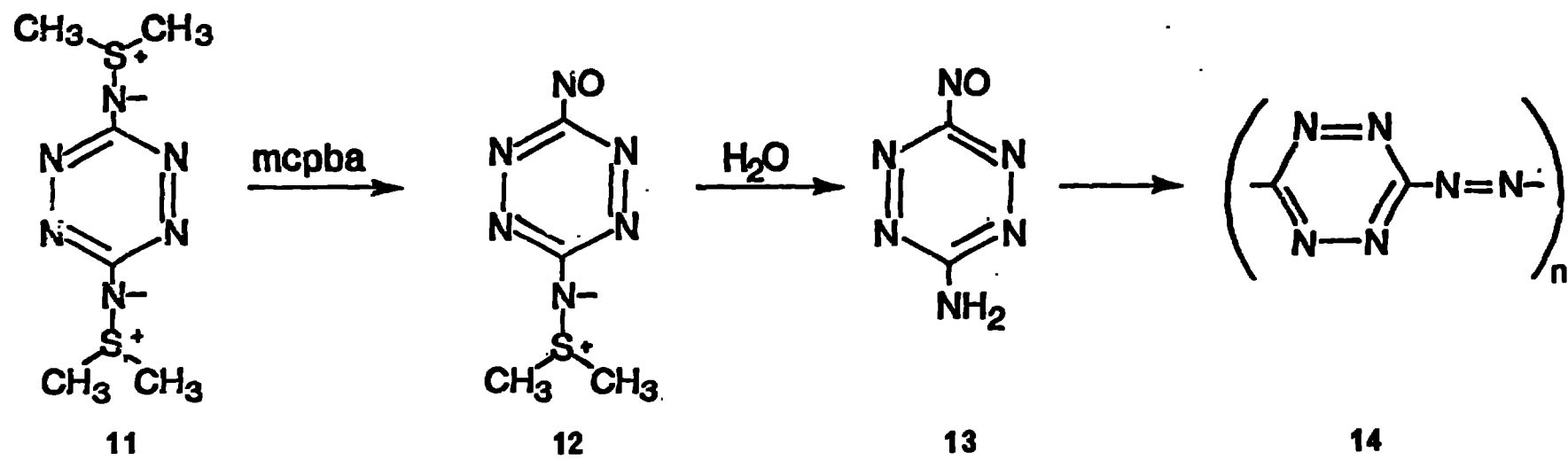


Fig. 4