Oxidation of Heterocyclic Nitrogen Ylids to Nitro Heterocycles. Comparison of Dimethyldioxirane with Peracids

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Oxidation of 3-amino-4-(4-chlorophenyl)furazan (**1**) and its phosphine imine derivative, 3-(4-chlorophenyl)-4-trioctylphosphiniminofurazan (**3**), with dimethyldioxirane (DMD) gave 3-(4-chlorophenyl)-4-nitrofurazan (**4**) as the exclusive product. However, the sulfilimine derivative, 3-(4-chlorophenyl)-4-dimethylsulfiliminofurazan (**2**), was converted by DMD to the sulfoximine, 3-(4-chlorophenyl)-4-dimethylsulfoximinofurazan (**6**). These results contrast dramatically with the oxidations of these compounds with peracids.

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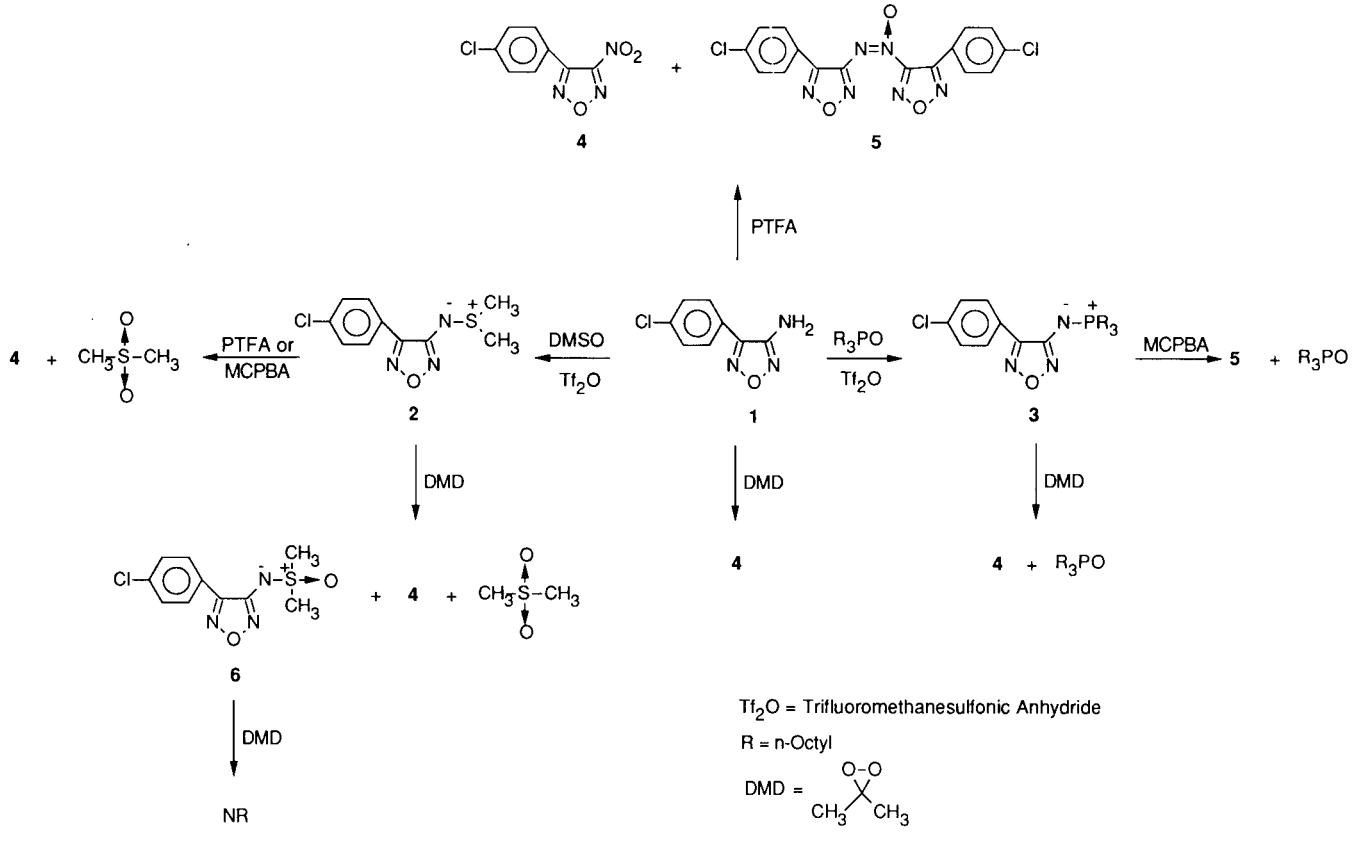
The oxidations of 3-amino-4-(4-chlorophenyl)furazan (**1**) and its sulfilimine (**2**) and phosphine imine (**3**) derivatives with peracids were reported in a previous communication from this Laboratory [1]. Thus, it was found that **1** reacted with peroxytrifluoroacetic acid (PTFA) in dichloromethane to give a mixture of 3-(4-chlorophenyl)-4-nitrofurazan (**4**) and azoxy(4-chlorophenylfurazan) (**5**) in 11% and 32% yields, respectively. Treatment of 3-(4-chlorophenyl)-4-dimethylsulfiliminofurazan (**2**) with either PTFA or *m*-chloroperoxybenzoic acid (MCPBA) gave **4** with no trace of **5**. In contrast, 3-(4-chlorophenyl)-4-trioctylphosphiniminofurazan (**3**) was recovered unchanged after treatment with PTFA, but was converted to **5** with no trace of **4** when treated with excess MCPBA.

Subsequent reports by Murray, *et al.* indicate dimethyldioxirane (DMD) to be a very powerful oxidant that is useful for the conversion of aliphatic and aromatic amines to the corresponding nitro compounds [2,3]. It therefore became of interest to compare the action of DMD on **1**, **2** and **3** with that of the peracids studied previously. Treatment of **1** with a ten-fold excess of DMD gave **4** as the exclusive product, with no trace of **5**. In contrast to the results obtained with MCPBA, treatment of **3** with a ten-fold excess of DMD also gave **4** as the exclusive product according to ^{1}H- and ^{13}C-nmr analysis, although a trace of **5** was detected by thin layer chromatography (tlc).



However, the most surprising result was the oxidation of **2** with a ten-fold excess of DMD to yield 3-(4-chlorophenyl)-4-dimethylsulfoximinofurazan (**6**) (63%) along with **4** (37%). When **2** was treated with a two-fold excess of DMD, pure **6** was obtained in 48% yield after two recrystallizations. Pure **6** was recovered unchanged after treatment with excess DMD; therefore, **6** is not intermediate in the formation of **4**. It is likely that **2** was partially hydrolyzed to **1** by residual water in the DMD solution, although the solution was dried over 4A molecular sieves prior to use. The **1** thus formed would be oxidized to **4** by DMD. The oxidation of **2** by a wet DMD solution to give only 36% of **6** along with 64% of **4** supports this explanation.

It is difficult to offer a rigorous explanation for the profound differences found in the oxidations of **1**, **2** and **3** with DMD as compared with the peracids studied previously, since the oxidants are all considered oxygen-transfer agents. Other than oxidizing strength, the major difference between these oxidants is acidity: DMD is neutral while the peracids are acidic, although MCPBA is a very weak acid. Hopefully, as DMD is more fully characterized and studied a reasonable explanation for these results will be evident.

EXPERIMENTAL

Melting points were determined with a Mettler FP1 apparatus and are corrected. The nmr spectra were recorded on a JEOL-FX90Q spectrometer. Elemental analyses were performed M. J. Naranjo, Los Alamos National Laboratory.

Oxidations with Dimethyldioxirane (DMD).

General Procedure.

To a freshly distilled solution [2] of DMD (~2 mmoles) in acetone (~25 ml) was added 4A molecular sieves. After storing in the freezer overnight, the solution was treated with the substrate (0.2 mmole) and the resulting mixture allowed to stand at ambient temperature for 16 hours. After the sieves were removed by filtration, the solution was analyzed by thin layer chromatography (tlc), then evaporated to dryness under reduced pressure. The residue was taken up in deuteriochloroform (0.5 ml) and analyzed by ^{1}H- and ^{13}C-nmr spectroscopy.

A. 3-Amino-4-(4-chlorophenyl)furazan (**1**) [1].

Analysis by both ^{1}H- and ^{13}C-nmr spectroscopy showed the residue to contain only 3-(4-chlorophenyl)-4-nitrofurazan (**4**) [1]. In addition, tlc showed no trace of azoxy(4-chlorophenylfurazan) (**5**) [1].

B. 3-(4-Chlorophenyl)-4-dimethylsulfiliminofurazan (**2**) [1].

Analysis of the residue by ^{1}H-nmr showed that 63% of the **2** was converted to 3-(4-chlorophenyl)-4-dimethylsulfoximinofurazan (**6**) and 37% was converted to an equimolar mixture of **4** and methyl sulfone. Confirmation of the assignments of **4**, **6** and methyl sulfone was obtained by ^{13}C-nmr.

Another reaction was performed in which the DMD solution was not treated with 4A sieves. In this case the product distribution was **4** (64%) and **6** (36%).

C. 3-(4-Chlorophenyl)-4-dimethylsulfoximinofurazan (**6**).

Analysis by ^{1}H- and ^{13}C-nmr spectroscopy as well as tlc showed the residue to be exclusively unchanged **6**.

D. 3-(4-Chlorophenyl)-4-trioctylphosphiniminofurazan (**3**) [1].

Analysis of the residue by ^{1}H- and ^{13}C-nmr spectroscopy showed only peaks corresponding to **4** and trioctylphosphine oxide; however, tlc showed a trace of **5**.

Preparation of 3-(4-Chlorophenyl)-4-dimethylsulfoximinofurazan (**6**).

To a freshly distilled solution [2] of DMD (~ 2 mmoles) in acetone (~25 ml) was added 4A molecular sieves. After storing in the freezer overnight, the solution was treated with **2** (0.26 g, 1.0 mmole) and the resulting mixture allowed to stand at ambient temperature for 16 hours. After the sieves were removed by filtration, the solution was evaporated to dryness under reduced pressure. Integration of the methyl protons in the ^{1}H-nmr spectrum indicated 87% conversion of **2** to **6**, with the remainder going to methyl sulfone. The aromatic region was very messy, which suggests a variety of minor products. Analysis by tlc showed **4**, **5** and another unidentified compound, possibly the nitroso precursor of **4**, to be present. Recrystallization of the residue from aqueous methanol, then from chloroform/hexane gave pure **6** (0.13 g, 48%), mp 156°; ^{1}H-nmr (deuteriochloroform): δ 3.40 (s, 6H), 7.41 (d, J = 8.5 Hz, 2H), 8.08 (d, J = 8.5 Hz, 2H); ^{1}H-nmr (methyl sulfoxide-d_6): δ 3.52 (s, 6H), 7.60 (d, J = 8.5 Hz, 2H), 8.15 (d, J = 8.5 Hz, 2H); ^{13}C-nmr (deuteriochloroform): δ 42.1, 124.8, 129.0, 136.4, 148.0, 154.0; ^{13}C-nmr (methyl sulfoxide-d_6): δ 41.1, 124.7, 129.0, 129.2, 135.3, 147.6, 154.2.

Anal. Calcd. for $C_{10}H_{10}ClN_3O_2S$: C, 44.20; H, 3.71; N, 15.46. Found: C, 44.39; H, 3.62; N, 15.47.

Acknowledgement.

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REFERENCES AND NOTES

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