

First Synthesis of Tetrachloropyrazine Bis-*N*-Oxide

Demetrios Kyriacou

Research Laboratories, The Dow Chemical Company, Western Division,  
Pittsburg, California 94565

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Sir:

The literature contains no information on the existence or synthesis of tetrachloropyrazine bis-*N*-oxide. The present communication is the first report concerning the above substance.

In general, formation of *N*-oxides of polyhalogenated aromatic-*N*-heterocycles requires quite vigorous conditions. Usually organic peracids are the oxidizing agents (1,2).

The mono-*N*-oxide of tetrachloropyrazine (and of several polyhalogenated aromatic amines) can be prepared by using trifluoroacetic acid and hydrogen peroxide as an oxidizing medium (3); the bis-*N*-oxide of tetrachloropyrazine, however, can not be prepared even when 90% hydrogen peroxide in the above acid is used (temperatures above 50-60° can not be effectively employed because of peroxide decomposition).

It was found that in a medium made by mixing concentrated sulfuric acid and 60% hydrogen peroxide conversion of tetrachloropyrazine to bis-*N*-oxide up to ca. 70% can take place at room temperature with only a small molar excess of hydrogen peroxide relative to tetrachloropyrazine bis-*N*-oxide to be formed. In a typical experiment, 40 g. (0.185 mole) of tetrachloropyrazine was dissolved in 240 ml. of 96% sulfuric acid (reagent grade), and to this solution was added over a period of 10 minutes, 24 ml. of 60% hydrogen peroxide, not allowing the temperature to go above 30°. The reaction was then allowed to take place at 22 to 23° for ca. 20 hours. The reaction mixture was then diluted with 800 ml. of ice-cold water and the copiously produced crystals were collected by filtration and washed free of acid. This solid product consisted of ca. 70% bis-*N*-oxide and ca. 30% of mono-*N*-oxide of tetrachloropyrazine and a small amount of the

initial tetrachloropyrazine. Separation of the bis-*N*-oxide from the mixture was effected by boiling the solid mixture three times with 500 ml. of acetone each time and decanting the supernatant acetone phase. The acetone insoluble solids was the desired bis-*N*-oxide, 99.5% pure (4); it is a pale white crystalline substance, melting at ca. 310° with decomposition. The material is only sparingly soluble in methanol, acetone, benzol, dichloromethane and methyl ethyl ketone (0.5-1 g. per liter). In sulfolane more than 15 g. per liter may dissolve at 28°.

During reaction the mono-*N*-oxide forms first, much faster than the bis-*N*-oxide. If one mole of hydrogen peroxide per mole of tetrachloropyrazine is used only the mono-*N*-oxide is obtained. No bis-*N*-oxide forms if the initial sulfuric acid is less than 90% (hydrogen peroxide 60%). In such cases only the mono-*N*-oxide may be produced. It is believed at this juncture that the effective agent to give bis-*N*-oxide is the *in situ* formed Caro's acid, persulfuric acid.

## REFERENCES

- (1) E. Ochiai, "Aromatic Amine Oxides", Elsevier, Amsterdam, 1967.
- (2) G. H. Chivers and H. Suschitzky, *Chem. Commun.*, 29, (1971).
- (3) Unpublished work by Dr. Howard Johnston, The Dow Chemical Co., Walnut Creek, Calif.
- (4) Analysis and confirmation of bis-*N*-oxide was made by infrared and mass spectroscopy, thin layer chromatography and elemental analysis. *Anal. Calcd.* for C<sub>4</sub>Cl<sub>4</sub>N<sub>2</sub>O<sub>2</sub>: C, 19.23; Cl, 56.75; N, 11.21; O, 12.81. *Found*: C, 19.27; Cl, 56.58; N, 11.05; O, 13.10.