The samples were run as neat liquids, in standard NMR tubes, taken directly from the reaction mixtures. In cases where exact NMR data were required, tetramethylsilane was added as an internal standard.

Benzyl bromide and sodium cyanide were used as starting materials for the production of benzyl cyanide.<sup>1</sup> The crude benzyl cyanide was then reacted with bromine vapor.<sup>2</sup> The hydrogen bromide that was produced was flushed from the reaction mixture with either nitrogen or air. Products that have been positively identified from the reaction mixture by means of mass spectrometry, proton NMR, and ir, were  $\alpha$ -monobromobenzylcyanide,  $\alpha,\alpha$ -dibromobenzylcyanide, diphenylmaleicnitrile, and  $\alpha$ -bromophenylacetyliminobromide. Benzyl cyanide and benzyl chloride were also present as unreacted compounds. The  $\alpha$ -bromophenylacetyliminobromide<sup>3</sup> was insoluble in the liquid phase of the other compounds and can be determined gravimetrically.

Proton NMR was used in order to determine molar percentages of the remaining compounds (Table I). An integration of the peaks in the spectra provided quantitative data on the molar percentages of benzyl cyanide, benzyl chloride, and  $\alpha$ -monobromobenzyleyanide. After the contributions of these compounds were subtracted from the phenyl absorption, the molar percentage of  $\alpha,\alpha$ -dibromobenzylcyanide and diphenylmaleicnitrile was computed. The quantity of  $\alpha,\alpha$ -dibromobenzylcyanide relative to the quantity of diphenylmaleicnitrile can be determined by mass

## Near-Ultraviolet Absorption Spectrum of 5,10-Dihydrophenazine

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(Received 15 April 1968; revision received 13 June 1968)

In the course of other work <sup>1</sup> it became necessary to synthesize and determine the near-uv absorption spectrum of 5,10 dihydrophenazine. Since, to our knowledge the spectrum of this compound has not been reported previously, we wish to present our findings here.

*Experimental.* 5,10 dihydrophenazine was prepared from phenazine by a modification of the method of Scholl.<sup>2</sup> A solution of 40-g  $Na_2S_2O_4$  and 18-g NaOH in 600-ml absolute methanol was heated to reflux under an atmosphere of argon. Two and one-half grams of solid phenazine were slowly added and the spectrometry. The weight percentage of each substance was then calculated from the molecular weights of the compounds.

Several control samples approximating the constituents in a typical sample were prepared. NMR analyses run on the control samples have been accurate to within  $\pm 2\%$ .

The following is a typical sample from the reaction mixture analyzed:

Molar	percentage	$\mathbf{Compound}$
	1%	benzyl chloride
	4%	benzyl cyanide
	80%	$\alpha$ -monobromobenzylcyanide
	10%	$\alpha, \alpha$ -dibromobenzylcyanide
		diphenylmal eicnitrile
	5%	$\alpha$ -bromophenylacetyliminobromide.

Proton NMR has been found to be a rapid and an accurate means of investigating this reaction and similar reactions.

Hundreds of samples have been analyzed by this method.

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- E. R. Hayden and E. R. Powell, "Bromobenzyl Cyanide," 27 December 1916, File No. EAL-476, Edgewood Arsenal, Maryland.
- 3. N. Beitsch, Edgewood Arsenal Analytical Research Department, (private communication).

mixture refluxed overnight. The entire reaction flask was then sealed with stoppers and transferred to a glove bag which was flushed six times with argon. Approximately 1 liter of water was then added to the reaction mixture. The water had been previously deoxygenated by standing over Na<sub>2</sub>SO<sub>3</sub> and NaOH for 24 h in a sealed flask. The mixture was filtered and the precipitate washed three times with 300-ml portions of deoxygenated water. The product was sucked as dry as possible, then transferred to a small vial which was placed into a vacuum drying pistol. The drying pistol was evacuated, removed from the glove bag, and the dihydrophenazine dried at 100° in vacuum over anhydrone. The white powder obtained was stable for periods of up to several months in a sealed container under argon. Contact with air while the powder was moist caused the dihydrophenazine to turn the dark green color attributed to solid complexes of phenazine and dihydrophenazine of varying stoichiometry.<sup>3</sup>

Attempts to obtain the melting point of the dihydrophenazine in sealed capillary tubes under vacuum, argon, or nitrogen were unsuccessful owing to decomposition of the sample. In every case decomposition began at temperatures higher than 220° (reported m.p. of dihydrophenazine, 317°).<sup>2</sup> The

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Fig. 1. Absorption spectra of phenazine and 5,10 dihydrophenazine. (1) \_\_\_\_\_\_ Composite spectrum (spectrum A); (2) ---⊕--- phenazine (spectrum B); (3)---●---5,10 dihydrophenazine.

mass spectrum of dihydrophenazine was identical with that of phenazine as would be expected from the easy loss of the two hydrogen atoms upon ionization. The ir spectrum of dihydrophenazine in a KBr matrix is essentially identical with that of phenazine, except for a sharp band at 3390 cm<sup>-1</sup> in the N-H stretching region and a band at 1505 cm<sup>-1</sup> in the N-H bending region.

Results. Since dihydrophenazine is extremely airsensitive, a special procedure was necessary to prepare solutions for obtaining uv spectra. Approximately 150-cc absolute methanol were placed in a bulb on a vacuum line. A few pellets of NaOH and 2-3 g Na<sub>2</sub>SO<sub>3</sub> were added and the system was sealed off. The methanol was degassed by the conventional freeze-pump-thaw technique several times, then sealed off, and permitted to stand over the Na<sub>2</sub>SO<sub>3</sub>-NaOH for several days. Just before it was to be used, the methanol was distilled into the receiving bulb by bulb-to-bulb distillation and sealed off by collapsing the walls of the glass tubing while the system was under vacuum. The oxygen-free methanol was transferred to a glove bag which was flushed several times with argon. A sealed capillary tube containing dihydrophenazine was opened and the contents placed into a dry flask. The bulb containing degassed methanol was opened and poured into the flask. The flask was stoppered and inverted several times, and the undissolved dihydrophenazine was permitted to settle out. The solution was then removed with a hypodermic syringe and placed into spectrophotometer cells with path lengths of 0.1, 1, and 10 cm. The cells were tightly sealed with Teflon stoppers, removed from the glove bag, and spectra were run as quickly as possible (less than 15 min elapsed from the time the cells were removed from the glove bag until the spectra were completed) (spectrum A). The cells were then opened to the air and another spectrum run (spectrum B).

The composite spectrum of phenazine and dihydrophenazine (referred to as spectrum A) and the individual components are shown in Fig. 1. The dihydrophenazine spectrum shows a maximum at 29,800 cm<sup>-1</sup> (325 m $\mu$ ) (log  $\epsilon = 3.8$ ).

Because it was impossible to assure the removal of all traces of oxygen, spectrum A is a composite spectrum of phenazine and dihydrophenazine. The dihydrophenazine component may be separated from the phenazine component by assuming that dihydrophenazine absorbs at shorter wavelengths than phenazine. If this assumption is valid, the ratio of spectrum A to spectrum B should be constant at long wavelengths. This condition was found to exist for  $\nu \geq$ 25,600 cm<sup>-1</sup> (390 m $\mu$ ). A constant fraction of spectrum B was then subtracted from spectrum A to obtain the dihydrophenazine spectrum.

This work was supported in part through funds provided by the U. S. Atomic Energy Commission under Contract AT(30-1)-905.

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## Determination of Magnesium in Vomitus by Atomic Absorption Spectrophotometry and EDTA Titration

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(Received 10 May 1968; revision received 22 July 1968)

During a research study to compare the effectiveness of two pharmacologic emetics,<sup>1</sup> it was found necessary to determine magnesium in vomitus. Pediatric patients who had ingested various poisons were randomly given the test emetics. One gram of magnesium hydroxide was given before induction of emesis. Total vomitus was collected and forwarded to this laboratory to determine percent recovery of magnesium hydroxide.

Table I. Atomic absorption operating conditions.

Burner Lamp Lamp current Elevator position Operation Number of passes Support gas Fuel gas Support gas setting Fuel gas setting Aspiration rate Slit Wavelength	Laminar flow Hollow cathode, magnesium 10 mA 0.4 in. Cold 1 Air Acetelyne 18 psi 5 psi 5 psi 5 ml/min. 0.2 mm 285.2 µ