curials gave variable results as much as 77% too high when analyzed here by the Vieböck–Schwappach method[3] and also in a commercial laboratory. It was obvious that the fault lay with the compounds when analysis of the hydroxymercurials showed an apparent methoxyl content of a few per cent. A suspicion that this error was caused by co-distillation of methyl and butyl iodides was confirmed by analysis of n-butyl o-methoxybenzoate (VII); this compound gave consistent results indicating two alkoxyl groups per mole. The n-butyl iodide which must have carried over in this last methoxyl determination to give such high results was actually isolated (49% yield) in a comparable macro-experiment and identified by conversion to n-butyl S-isothiourea picrate, m. p. 174.[4] Although it was not possible to isolate butyl halide from the analyses of III, IV, V and VI, there is little doubt that the methoxyl analyses of these are in error from the same cause.

The difficulty could be partly though not wholly avoided by elimination of the phenol ordinarily used in this determination.[5] Under these conditions the methoxymercurials gave values only 4% too high, while VII gave apparent methoxyl values between one and two groups per mole. Similar discrepancies have been noted before.[6] It seems necessary to question the reliability of the usual analytical procedure, not only with compounds where other alkoxyl groups are present, but also, as in the case of the methoxymercurials, where there exists any possibility that other alkyl halides may be formed.

Acknowledgment.—The authors are grateful for the generosity of the authors of reference 2 in making samples of 2-butene available. They wish to express their thanks also to Miss J. Romeyn and Miss G. Stonestreet for assistance in the microanalyses and to Dr. G. F. Wright for his helpful advice throughout this work.

Summary

1. The methoxy- and hydroxy-mercurials of cis- and trans-2-butene have been prepared.

2. The rates of mercuration indicate that the low-boiling 2-butene has the trans configuration.

3. Errors in methoxyl determinations have been shown and corrected.

(3) (a) Vieböck and Brecher, Ber., **63**, 3207 (1930); (b) Vieböck and Schwappach, ibid., **63**, 2818 (1930).

(4) Brown and Campbell, J. Chem. Soc., 1699 (1937).

(5) (a) Friedrich, "Die Praxis der quantitativen Mikroanalyse," F. Deuticke, Leipzig; (b) Wright and Hibbert, THIS JOURNAL, **59**, 125 (1937).

(6) King, ibid., **61**, 2383 (1939).

Ultraviolet Absorption in a Series of Chloropyrimidines in the Vapor State and in Solution

BY FRED M. UBER AND ROGER WINTERS

In view of the importance of compounds which contain the pyrimidine ring in their structure, it is desirable to have more knowledge concerning the absorption spectra of pyrimidine itself and of its simpler substitution products. Moreover, recent progress in the interpretation of the spectra of benzene and pyridine make it appear hopeful that the spectrum of a six-membered heterocyclic ring with two nitrogen atoms might also be amenable to analysis. With the great interest in the correlation of absorption spectra and chemical constitution, as evidenced in several recent papers,[1] additional data on the behavior of absorption within a series of compounds should prove valuable.

Ultraviolet absorption measurements on solutions of various pyrimidine derivatives have been reported in two papers by Heyroth and Loofbourow,[2] who were able to correlate their spectra with the degree of saturation of the pyrimidine ring. It seemed evident from their published absorption curves that considerable fine structure must exist in spectra of the vapor state, particularly in pyrimidine, and this has now been confirmed.

The absorption behavior of a number of amino- and oxypyrimidines has been determined by Williams, Ruehle and Finkelstein.[3]

Experimental

Method.—As a source of continuous ultraviolet for the vapor spectra a hydrogen discharge tube has been used. The quartz spectrograph was a medium Hilger instrument. Quartz absorption cells for the vapor had lengths of 1.0, 3.0, and 11.0 cm. Side tubes permitted filling and sealing-off, the latter being done while maintaining a vacuum. Arrangements were made whereby the temperature of any cell could be varied in order to secure the most favorable conditions for photographing fine structure in the absorption spectra. Eastman "33" photographic plates were employed. The wave lengths were measured on tracings made with a Leeds and Northrup recording microphotometer.

(1) Smakula, Angew. Chem., **47**, 657 (1934); Dimroth, ibid., **52**, 545 (1939); Lewis and Calvin, Chem. Rev., **25**, 273 (1939).

(2) Heyroth and Loofbourow, THIS JOURNAL, **53**, 3441 (1931); ibid., **56**, 1728 (1934).

(3) Williams, Ruehle and Finkelstein, ibid., **59**, 526 (1937).

Molecular extinction coefficients, defined by $\epsilon = (1/cd)$ $\log_{10}(I_0/I)$ where d is in cm. and c is the concentration in moles/liter, were obtained with a Spekker photometer and an iron–tungsten spark source in conjunction with a medium Hilger spectrograph. Quartz absorption cells of 1.0 and 10.0 cm. length were used for solutions. In order to reveal structure in the solution spectra not shown by the spark source, photographs were made using the continuous spectrum from a hydrogen discharge tube. In this latter case the Spekker photometer was not employed.

Materials.—The substances used were pyrimidine, 2,6-dichloropyrimidine, 2,4,6-trichloropyrimidine, and 2,4,5,6-tetrachloropyrimidine.

Pyrimidine was made by reducing trichloropyrimidine with zinc dust and water, according to the method of Gabriel.[4] It was rendered anhydrous with metallic potassium and purified by distillation. Owing to the difficulty of preparation, only small quantities were available. The m. p. of the purified pyrimidine was 21°, which agrees with the value given by Gabriel.

Dichloropyrimidine was prepared by the action of phosphorus oxychloride on uracil, as described by Gabriel.[5] The crude product was purified by distillation under a partial vacuum. The m. p. was 61°. Values of 59 to 62° are recorded in the literature.

Trichloropyrimidine was made from barbituric acid by the action of phosphorus oxychloride, using the method of Gabriel.[4] It was purified by distillation at atmospheric pressure and had a m. p. of 21°, which agrees with the value given by Gabriel.

Tetrachloropyrimidine was prepared by the action of phosphorus oxychloride and phosphorus pentachloride on dialuric acid, according to the method of Emery.[6] The dialuric acid was prepared from uric acid, using the method described by Biltz and Damm.[7] The tetrachloropyrimidine was purified by distillation under reduced pressure. It had a m. p. of 67°. Emery lists the m. p. as 68–70°.

An attempt to prepare a monochloropyrimidine by action of phosphorus oxychloride on 6-oxypyrimidine was not successful, possibly because of the small quantity of material available. The method tried was analogous to that used for preparation of the other members of the series.

Solutions.—Pyrimidine solutions in redistilled water were used in concentrations of 36.0, 48.0, and 72.0 mg./liter, and in both 1.0 and 10.0 cm. cells. Dichloropyrimidine was dissolved in pure methyl alcohol in a concentration of 40.0 mg./liter, and was placed in a 1.0 cm. cell. The trichloropyrimidine was dissolved in a 4% methyl alcohol–water mixture at a concentration of 39.2 mg./liter, and was used in a 1.0 cm. cell. The tetrachloropyrimidine was dissolved in a mixture of one-third methyl alcohol and two-thirds water, at a concentration of 35.6 mg./liter, and was used in a 1.0 cm. cell. In addition, absorption photographs were made, using a continuous spectrum, of a dilute aqueous solution of the mercuric chloride addition compound of pyrimidine.

Results and Discussion

Vapor Spectra.—The microphotometer record for pyrimidine vapor is reproduced in Fig. 1, where five broad but distinct absorption bands appear. In addition, some 125 sharp line-like bands occur in the 2800–3300 Å. region (not illustrated). A more detailed study of the latter, using a grating, has been planned. These sharp bands correspond to a similar system reported for pyridine from 2700–3100 Å. by Henri and Angenot[8] and to the well-known system of benzene from 2200–2800 Å. Thus there is a progressive displacement toward longer wave lengths with the introduction of successive nitrogen atoms into the benzene ring.

With the substitution of two chlorine atoms on the pyrimidine ring, there is a marked change in absorption, the sharp bands in the long wave length region disappearing entirely. The broad bands, which correspond to those shown in Fig. 1 for pyrimidine, are reproduced in Fig. 2. There has been a shift of about 150 Å. toward longer wave lengths and some loss in structure.

On the microphotometer record of trichloropyrimidine, shown in Fig. 3, a further shift toward the red of some 40 Å. is evident. More bands are apparent in this compound, and the general appearance of the band has changed, the main peak becoming much narrower.

The most marked variation was encountered in the tetrachloropyrimidine, which shows numerous small and relatively sharp bands over a wide wave length region (upper curve of Fig. 4). In addition, there are some bands centering around 2730 Å., showing but little structure (lower curve of Fig. 4), but these are the bands that correspond to the ones already mentioned for other members of the series. This means, then, a further wave length shift of some 160 Å. toward the red.

It has been observed generally that an increase in molecular weight of a series of compounds produces a shift in the absorption spectra toward longer wave lengths. Specific examples have been recorded for pyridine and its derivatives by Purvis,[9] Purvis and Foster,[10] and Baker and Baly.[11] In the chloropyrimidines, the shift between pyrimidine and dichloropyrimidine, which represents two steps in the series, is relatively greater than the shift between the di- and trichloroderivatives.

(4) Gabriel, *Ber.*, **33**, 3666 (1900).

(5) Gabriel, *ibid.*, **38**, 1689 (1905).

(6) Emery. *ibid.*, **34**, 4178 (1901).

(7) Biltz and Damm, *ibid.*, **46**, 3662 (1913).

(8) Henri and Angenot. *Compt. rend.*, **201**, 895 (1935).

(9) Purvis, *Proc. Cambridge Phil. Soc.*, **14**, 435 (1907–1908).

(10) Purvis and Foster, *ibid.*, **14**, 381 (1907–1908).

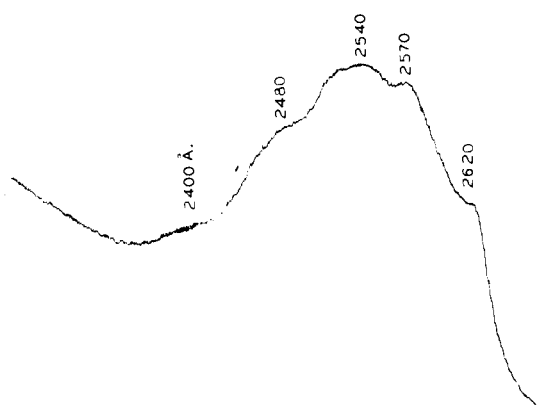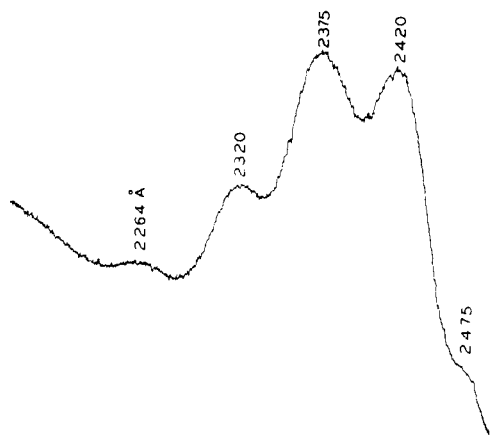(11) Baker and Baly, *J. Chem. Soc.* (Trans.), **91**, 1122 (1907).

Fig. 1.—Microphotometer tracing of absorption spectrum of pyrimidine vapor, 28°, 1-cm. absorption cell.

Fig. 2.—Microphotometer tracing of absorption spectrum of dichloropyrimidine vapor, 44.7°, 11-cm. cell.

It might be expected that the next step, between the tri- and tetrachloro-compounds, would be still smaller, but this is not the case. The relatively larger displacement found in the last member of the series may be analogous to a situation found by Conrad-Billroth[12] in the chlorobenzenes. Here it was shown that substitution into the para position caused a greater wave length shift toward the red than was produced by substitution into either the ortho or meta position. It will be noted that in 2,4,5,6-tetrachloropyrimidine the 2- and 5- chlorine atoms occupy para-positions.

Solution Spectra.—The molecular extinction coefficients of pyrimidine and of dichloropyrimidine in solution are plotted against wave length in Fig. 5, and a similar graph for the tri- and tetrachloro-derivatives is shown in Fig. 6. The data for these curves were obtained with a Spek-

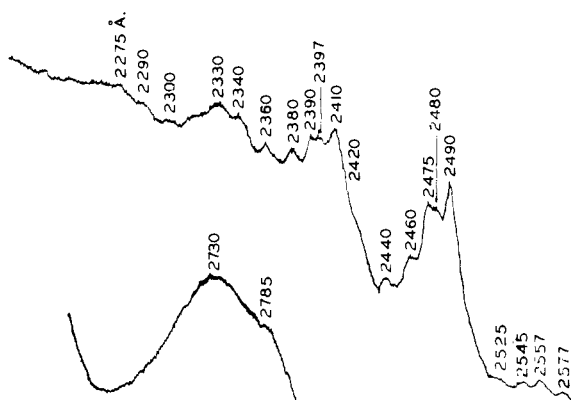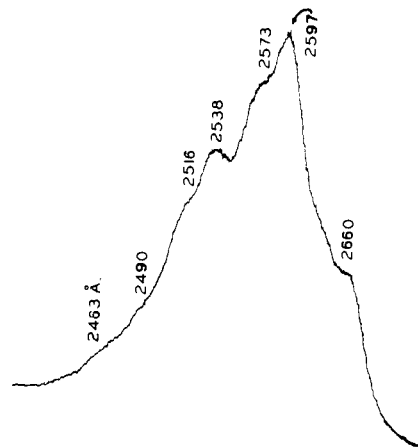(12) Conrad-Billroth. Z. physik. Chem., 19B, 76 (1932).

Fig. 3.—Microphotometer tracing of absorption spectrum of trichloropyrimidine vapor, 78.5°, 1-cm. cell.

Fig. 4.—Microphotometer tracing of absorption spectra of tetrachloropyrimidine vapor: upper curve, 33.5°, 11-cm. cell; lower curve, 57.5°, 11-cm. cell.

ker photometer and a spark source so that no fine structure is evident. However, it will be shown in a later paragraph that some structure does exist for the solutions.

The molecular extinction coefficients for pyrimidine and dichloropyrimidine have been reported previously by Heyroth and Loofbourow[2] so that the curves of Fig. 5 are included here primarily for comparison with the spectra of tri- and tetrachloropyrimidines in Fig. 6. There are minor discrepancies as to the magnitude of the coefficients between the data of Fig. 5 and the values of Heyroth and Loofbourow, the latter being somewhat higher at the principal maximum in each case but lower at other wave lengths. A part of this discrepancy is probably due to the method used, since the Spekker and spark source has not detected the fine structure which was
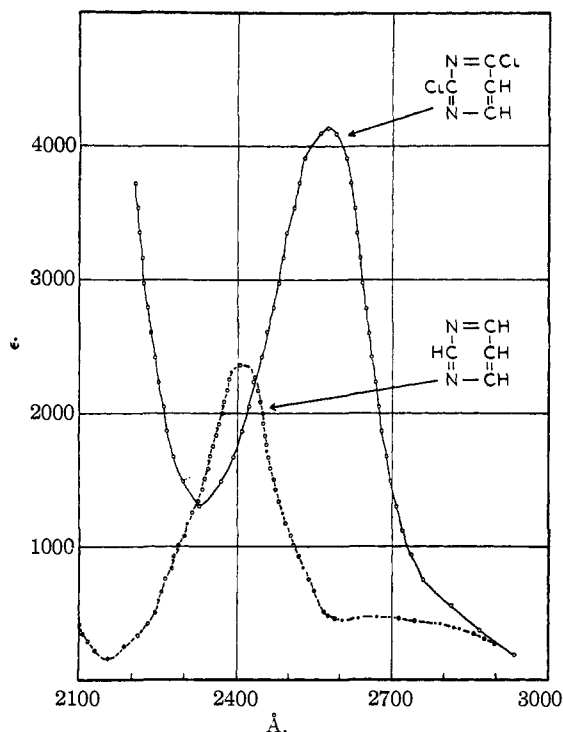
Fig. 5.—Molecular extinction coefficients for pyrimidine solution in water and dichloropyrimidine solution in methyl alcohol; Spekker photometer and spark source.
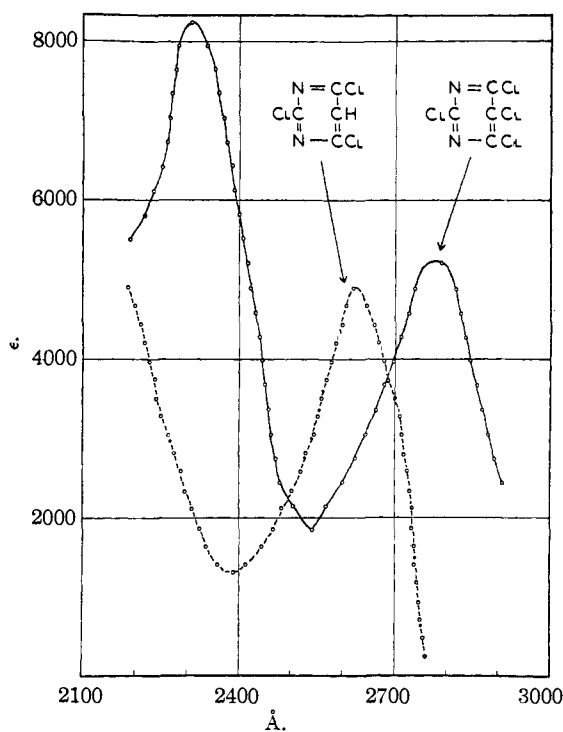

Fig. 6.—Molecular extinction coefficients for trichloro-pyrimidine solution in 4% methyl alcohol and tetrachloro-pyrimidine solution in one-third methyl alcohol, two-thirds water; Spekker photometer and spark source.

shown in the curves of Heyroth and Loofbourow.

The displacement of the region of maximum absorption toward the red with each additional chlorine atom in the molecule, as noted in the case of the vapor spectra, is again evident. In fact, the wave length shift is so marked that the appearance of a second absorption peak above 2300 Å. is to be noted in the case of tetrachloro-pyrimidine, whose absorption spectrum resembles quite closely that of vitamin B_1.[13] Increasing absorption in the neighborhood of 2100 Å. in the other three members of the series indicates that similar maxima might be found for them if the range of observation were extended to still shorter wave lengths.

In addition to the wave length shift, there is a marked increase in the maximum molecular extinction coefficient as the chlorine content of the molecule increases. A similar situation was noted by Conrad-Billroth[12] in the chlorobenzene series up to the pentachloro-derivative.

The location of the absorption bands in the pyrimidine–mercuric chloride addition compound is about 40 Å. further toward the red than that of

the corresponding bands in pyrimidine itself. This shift may be attributed to the increased molecular weight. The effect is not very large, considering the added weight, but it is to be remembered that this is an addition compound, while the others are substitution compounds with the increased weighting attached directly to the pyrimidine ring.

Effect of pH.—Solutions of pyrimidine and tetrachloropyrimidine were also made in 0.0001 N hydrochloric acid and in 0.00001 N potassium hydroxide, and the extinction coefficients determined. In all four cases, neither the amount of absorption nor the location of maxima was significantly different from that in neutral solution. This differs from the 6-aminopyrimidines, where Williams, Ruehle, and Finkelstein[3] found two absorption maxima for basic solutions but only one maximum for an acid solution. The same behavior characterizes vitamin B_1.[14]

Fine Structure.—Spectrograms made with a continuous source revealed more structure than is apparent in the Spekker curves of Figs. 5 and 6, which were obtained with the aid of a spark.

(13) Wintersteiner, Williams and Ruehle, This Journal, **57**, 517 (1935).

(14) Uber and Verbrugge, J. Biol. Chem., **134**, 273 (1940).

Microphotometer records of these have not been reproduced here since they make no new contribution to the absorption picture as presented for the vapor state. It is to be noted that the findings of Heyroth and Loofbourow[2] with respect to fine structure in pyrimidine have been confirmed.

Absorption maxima were found at the following wave lengths: for pyrimidine at 2326, 2375, 2427 and 2483 Å.; for pyrimidine–mercuric chloride compound at 2357, 2412 and 2475 Å.; for dichloropyrimidine a broad band covering approximately 2470–2630 Å. with its center at 2540 Å.; for trichloropyrimidine at 2575, 2633 and 2695 Å.; for tetrachloropyrimidine at 2690, 2760 and 2870 Å. Microphotometer traces of the spectrum plates resembled those obtained when the vapors of the corresponding substances were photographed. In case of the solutions, however, the curves were in general flatter, the major peaks less well differentiated, and the smaller peaks often absent. The sharp line-like bands seen in the pyrimidine vapor spectrum did not appear in the photographs of the solution; neither did the group of relatively sharp bands of tetrachloropyrimidine in the 2200–2500 Å. region.

The writers wish to express their indebtedness to Dr. Victor R. Ells for assistance in the analysis of the Spekker plates for the solutions.

Summary

1. The ultraviolet absorption spectra of pyrimidine, dichloropyrimidine, trichloropyrimidine, and tetrachloropyrimidine have been photographed in the vapor state. All of these compounds exhibit a system of broad bands in the range 2300–2800 Å.

2. Pyrimidine shows some 125 sharp line-like bands in the 2700–3300 Å. region.

3. Molecular extinction coefficients in the range 2100–3000 Å. have been determined for solutions of pyrimidine, dichloropyrimidine, trichloropyrimidine, and tetrachloropyrimidine. Structure in the absorption bands, as observed in the vapor state, is still evident in solution, but is not so marked.

4. Absorption maxima shift progressively to longer wave lengths with successive increases in the number of chlorine atoms attached to the pyrimidine ring; corresponding increases in the magnitude of the molecular extinction coefficients also accompany the addition of successive chlorine atoms.

Catalytic Oxidation of Phosphorus Tribromide

BY C. R. JOHNSON AND L. G. NUNN, JR.

A number of methods are available for the preparation of phosphorus oxybromide, but none of them is particularly convenient or economical: it is perhaps significant that this compound is not found in most price lists of chemical reagents. The direct oxidation of phosphorus tribromide suggests itself as a convenient means of preparing the substance, but no reaction occurs when oxygen and the tribromide are mixed, at temperatures up to the boiling point of the latter. It has been stated that phosphorus oxybromide is formed by the action of oxygen on the tribromide at its boiling point.[1] This cannot be recommended as a method of preparation, as the reaction is not easy to control and sometimes goes explosively. Moreover, there seems to be some doubt whether

any appreciable amounts of POBr₃ are formed in the explosion, in which phosphorus pentoxide and bromine are also obtained.[2] Geuther and Michaelis[3] attempted to prepare the bromine analog of P₂O₃Cl₄ by the action of gaseous N₂O₃ and N₂O₄ on well-cooled liquid PBr₃, and note briefly that they obtained POBr₃ and P₂O₅ in the reaction.

We have found that in the presence of nitrogen oxides and oxygen, over a somewhat limited range of conditions, phosphorus tribromide vapor may be oxidized smoothly and non-explosively. Enough phosphorus oxybromide has been isolated from the reaction products in trial experiments to warrant the hypothesis that it is the main product of the non-explosive oxidation, and that the

(1) Demole, Bull. soc. chim., [2] 34, 201 (1880).

(2) Christomanos, Z. anorg. allgem. Chem., 41, 276 (1904).

(3) Geuther and Michaelis, Ber., 4, 766 (1871).