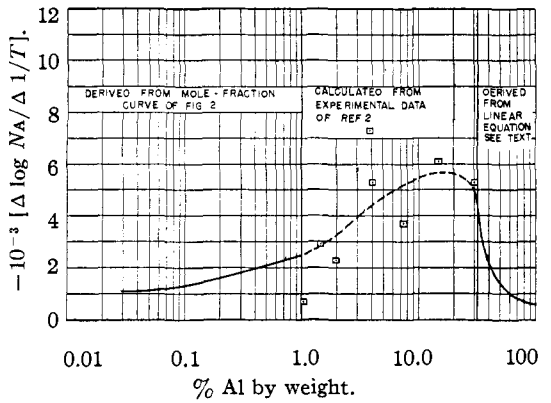


Fig. 3.—Variation of apparent heat of fusion with composition.

expresses the results of Smits and de Gruijter[1a] (*cf.* ref. 4, Fig. 59). In the intermediate region, where the mole-fraction curve has an inflection point, it seemed best to calculate ordinates directly from the experimental results of Klemm and Weiss.[2]

In the aluminum-rich region, the ordinate of Fig. 3 corresponds very closely to +2550 cal., the heat of fusion recommended for aluminum by Kelley.[5] (+2547 cal. was calculated for the interval 90–100% Al.) The pronounced variability over the rest of Fig. 3 may be due to variations in the activity coefficients, to changes in the composition of the solid in equilibrium, or to both.

I wish to thank my colleagues, Messrs. F. J. Norton and R. H. Harrington for permission to publish their two experimental results, and Mr. K. Berman for helping with the calculations.

Summary

1. The aluminum–mercury liquidus curve has been completed by the making of measurements designed to give good results with dilute aluminum amalgams.

2. Within the temperature range 76–312°, the per cent. by weight of aluminum "soluble" in mercury is given by the equation $\log_{10} s = 1.240 - (1132/T)$ to within about 10%.

3. The apparent heat of fusion in this system passes through a maximum as the aluminum content is increased. In nearly pure aluminum, the value of this heat agrees remarkably well with the heat of fusion recommended by Kelley for this element.

SCHENECTADY, NEW YORK

RECEIVED SEPTEMBER 14, 1948

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE INSTITUTUM DIVI THOMAE AND THE DEPARTMENT OF CHEMISTRY, SIENA HEIGHTS COLLEGE]

The Ultraviolet Absorption Spectra of Some Pyrimidines. Chemical Structure and the Effect of *p*H on the Position of $\lambda_{max.}$[1]

BY MIRIAM MICHAEL STIMSON[2]

It has been suggested by Brooker[3] that symmetrical ions should be more stable than unsymmetrical ones. So far this has not been demonstrated experimentally although symmetrical dyes are more stable to *p*H changes than are unsymmetrical ones. In the following discussion an attempt will be made to correlate symmetry and *p*H response in a group of pyrimidines.

One of the most striking of the absorption characteristics of the pyrimidines is the effect of *p*H on the intensity and, frequently, on the position of the absorption maximum (λ_{max}). This change in the position of the absorption maximum with *p*H-($\Delta\lambda_{max}$) seems not to be solely dependent on the nature of the substituent on the pyrimidine ring, since barbituric acid[4] although having a pronounced change in the molar absorbancy index, shows no appreciable change in the position of λ_{max}, while uracil has $\Delta\lambda_{max}$ of 24 mμ. Again it may be noted that in the case of 2-hydroxy-4,6-diaminopyrimidine there is no appreciable change in the position of the absorption maximum with change in *p*H; such a change is observed with both cytosine and isocytosine. From these various types of response to change in *p*H it is suggested that the effect of *p*H might be empirically related to the symmetry of the molecule. Thus both barbituric acid and 2-hydroxy-4,6-diaminopyrimidine may be considered as symmetrical, if the plane of symmetry be imagined to pass through the 2,5-positions. On this basis the pyrimidines under consideration may be classified as symmetrical or unsymmetrical.

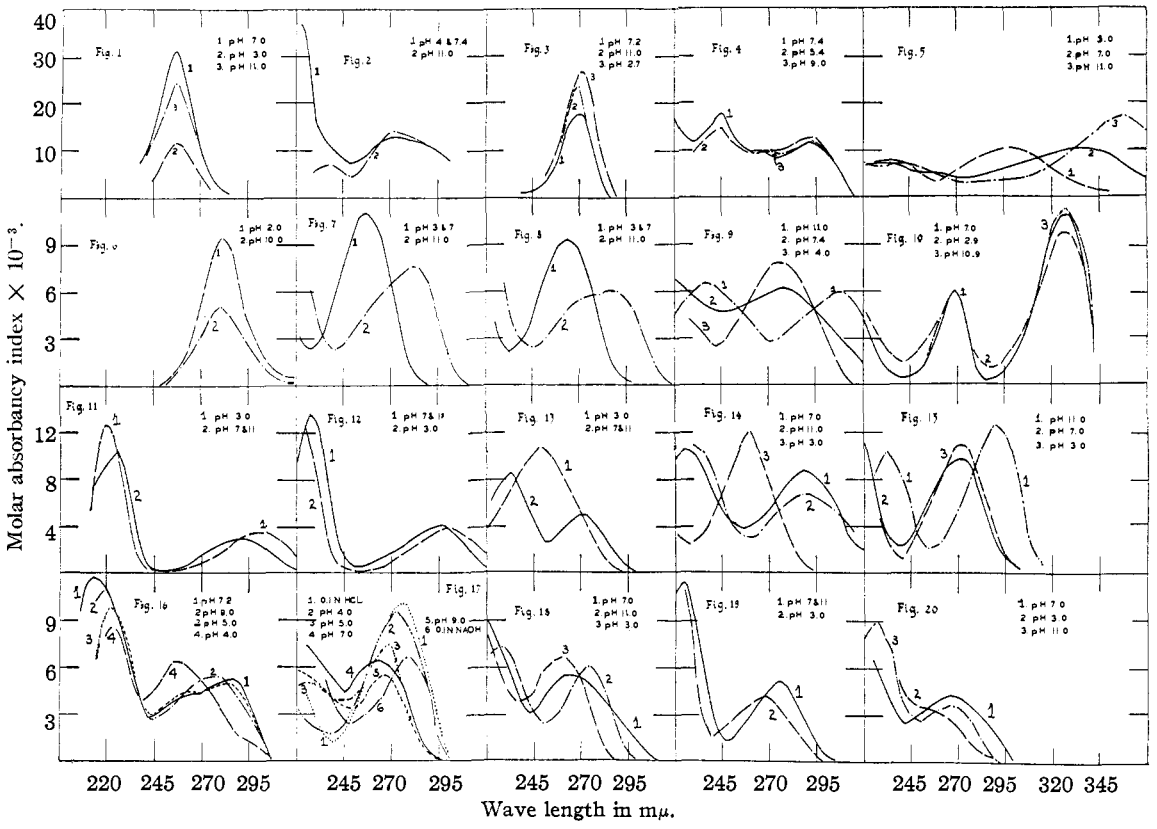
In Table I are listed seven pyrimidines, all of which are considered symmetrical with respect to the above mentioned plane. From the data presented the following empirical conclusions may be drawn: (1) The long wave absorption maximum of these compounds seems to be either unaffected or only slightly shifted by the *p*H values employed. (2) In either the 4,6-dihydroxy- or the 4,6-diaminopyrimidines, in which there is also a hydroxy

(1) From the dissertation presented to the faculty of the Institutum Divi Thomae in partial fulfillment of the requirements for the Ph.D., June 1948.

(2) Sister Miriam Michael Stimson, O.P.

(3) Brooker, "Resonance and Organic Chemistry" in "Advances in Nuclear Chemistry and Theoretical Organic Chemistry," ed. Burk and Grummitt, Interscience Publishers, Inc., New York, N. Y., 1945.

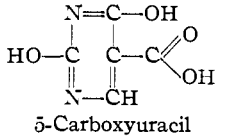
(4) Loofbourow and Stimson, *J. Chem. Soc.*, 1275 (1940); Stuckey, *Quart. J. Pharm. Pharmacol.*, **15**, 370 (1942).



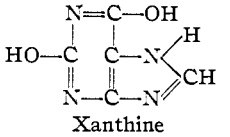
Figs. 1 to 20.—1, Barbituric acid; 2, 2-mercapto-4,6-dihydroxy-5-ethylpyrimidine; 3, 2-hydroxy-4,6-diaminopyrimidine; 4, 2-mercapto-4,6-diaminopyrimidine; 5, 5-nitrouracil; 6, 2-hydroxy-4,5,6-triaminopyrimidine; 7, uracil; 8, thymine; 9, isobarbituric acid; 10, 4,6-dihydroxypyrimidine; 11, 2-aminopyrimidine; 12, 2-amino-6-chloropyrimidine; 13, 2-chloro-6-aminopyrimidine; 14, 5-aminouracil; 15, 5-carboxyuracil; 16, isocytosine; 17, cytosine; 18, isocytosine-4-acetic acid; 19, 2-ethoxy-4-aminopyrimidine; 20, 2-methyl-4-hydroxy-6-ethoxypyrimidine.

group on the 2-position, the replacement of this hydroxy group by an –SH group is accompanied by the appearance of two maxima.[5] (3) The molar absorbancy index of an absorption band at any given *p*H apparently depends, within either a symmetrical or unsymmetrical structure, on the nature and number of the substituents, but auxochromes do not display their usual character when their introduction causes change from an unsymmetrical to a symmetrical structure. This can be seen by a comparison of both λ_{max} and $\Delta\lambda_{max}$ for cytosine, 2-hydroxy-4,6-diaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine.

Those compounds not symmetrical with respect to the 2–5 plane show sufficient uniformity to permit sub-classification. In Table II are listed the data for various uracil derivatives, all of which have the substituent on the 5-position. In these compounds the data may be considered under two aspects, namely, the modification of the absorption pattern of the parent compound, uracil, and the effect of *p*H on λ_{max}. The following conclusions may be drawn: (1) The introduction of the additional auxochrome on the 5-position causes an increased bathochromic shift when the *p*H is changed from 3 to 11. (2) There is a formal relationship in the spectral response of carboxyuracil and of xanthine.[6] Both show a single band in acid solution and both have two pronounced bands in basic solution. That this is not unreasonable may be inferred from the formal structural relationship which also exists between the two compounds. (3) The same sequence is given in either



5-Carboxyuracil



Xanthine

acid or basic solution by the various uracil derivatives if they are arranged in order of increasing wave length of the long wave maximum

(acid) $H{=}NH_3^+ < CH_3 < COOH < OH < NO_2$

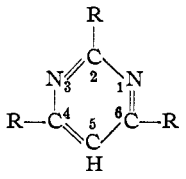
(basic) $H < NH_2{=}CH_3{=}COO^- < O^- < NO_2$.

The modification of the absorption spectrum shown by uracil may be, perhaps, more evident if $\Delta\lambda_{max}$ of uracil for the change from *p*H 3 to 11 be

(5) Fehnel and Carmack, at the Spring Meeting 1948, Chicago, reported a peak in the spectra of the alkylmercaptals at 235-240 mμ which corresponds to the short wave band in Figs. 2 and 4.

(6) Stimson and Reuter, THIS JOURNAL, **65**, 133 (1943).

TABLE I



Pyrimidine	Long wave band λmax, mμ	Long wave band Molar absorbancy index	Short wave band λmax, mμ	Short wave band Molar absorbancy index	pH	
Barbituric acid	257	550			1	*N* HCl
(2,4,6-trihydroxy-)	257	11000			3.0	
	257	31000			7.0	
	257	24500			11.0	
2-Thio-4,6-dihydroxy-5-ethyl-	273	14000	239	7050	4.0	
	273	13900	239	6600	7.4	
	273	12750	239	36700	11.0	
4,6-Dihydroxy-	328	8160	270	5050	2.9	
	328	9150	270	5000	7.0	
	328	9400	270	5120	10.9	
2-Hydroxy-4,6-diamino-	273	26500			2.7	
	270	17400			7.2	
	270	23300			10.9	
2-Hydroxy-4,5,6-triamino-	281	10000			0.1	*N* HCl
	281	9400			2.0	
	281	7400			6.4	
	281	5100			10.0	
	281	4700			11.0	
2-Thio-4,6-diamino-	286	25000	235	40950	0.1	*N* HCl
	291	12500	245	14000	5.4	
	292	11380	245	17800	7.4	
	292	14760	245	17200	9.0	
2-Thio-4,5,6-triamino-[a]	295	11900	245	13900	.....	

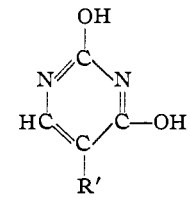
[a] Bendich, Tinker and Brown, THIS JOURNAL, **70**, 3109 (1948).

subtracted from the corresponding shift for each of the listed 5-uracil derivatives. If the log of the difference in the data between each of the uracils and uracil, respectively, be plotted against the dipole moment of the substituent, then practically a straight line relationship is obtained. The dipole moment data used are those listed in Landolt–Börnstein[7] for benzene derivatives. While these data do not accurately represent the values of the particular substituents in the uracil series, they may be considered as giving a relative evaluation. Of the six compounds tested only 5-carboxyuracil fails to show a difference in the shift of the absorption maximum as a regular function of the dipole moment. This failure of 5-carboxyuracil to respond as do the other uracil derivatives is not unreasonable in view of the formal structural and spectral similarities with xanthine.

In Table III are arranged the data of four 2-aminopyrimidines. In these compounds the upper half of the molecule is a substituted guanidine structure. The following observations may be made: (1) Each compound has two absorption bands. (2) The unsubstituted 2-aminopyrimidine and the derivative with a chlorine atom on the 6-position both show an increased separation of the absorption bands in acid solution as compared

(7) Landolt-Börnstein, "Physikalisch-chemische Tabellen," Eg. II, 74, 5th Umgearbeitete, 3rd Erganzungsband, 1st Teil, Edwards Brothers, Inc., Ann Arbor, Michigan, 1943.

TABLE II



Compound	Long wave band λmax, mμ	Long wave band Molar absorb. index	Short wave band λmax, mμ	Short wave band Molar absorb. index	pH	Δλmax,[a] mμ
Uracil	258	8600			3.0	24
(R′ = H)	258	8600			7.0	
	282	6400			11.0	
Thymine	264	7800			3.0	26
(R′ = CH_3)	264	7800			7.0	
	290	5100			11.0	
5-Amino-uracil	260	12200			3.0	30
	290	8600	225	10500	7.0	
	290	6700			11.0	
Isobarbituric acid	276	6600	222	4000	4.0	31
	278	5200	210	6600	7.4	
(R′ = OH)	307	4900	239	5300	11.0	
5-Nitro-uracil	300	10400	235	6880	3.0	58
	338	10600	235	7880	7.0	
	358	16750	240	6880	11.0	
5-Carboxy-uracil	270	11200	216	12500	3.0	30
	270	9800	216	11500	7.0	
	290	12800	232	10500	11.0	

[a] This is the change in $\Delta\lambda_{max}$ for the change from *p*H 3 to *p*H 11; *i. e.*, λ_{max} *p*H 11 − λ_{max} *p*H 3.

TABLE III

Compound	Long wave band λmax, mμ	Long wave band Molar absorb. index	Short wave band λmax, mμ	Short wave band Molar absorb. index	pH	Δλmax,[a] mμ
2-Amino-pyrimidine	300	3770	220	12600	3.0	
	290	2800	225	11000	7.0	−10
	290	2800	225	11000	11.0	
2-Amino-6-chloro-pyrimidine	300	4000			3.0	
	296	4200	229	13900	7.0	− 4
	296	4200	229	13900	11.0	
Isocytosine-4-acetic acid	259	6800			3.0	
	265	5700			7.0	+16
	275	6250			11.0	
Isocytosine	258	6300	223	8600	4.0	
	285	4950	222	9900	5.0	
	264	4700				
	285	5250	222	11700	7.2	
	267	4550				
	276	5500	218	10700	9.0	

[a] See note to Table II.

with basic solution. (3) The derivative with the hydroxy group on the 6-position shows the least separation of the two absorption maxima in solution at *p*H 4.0, and the greatest separation at *p*H 7.2, of the *p*H values tested.

4. Consideration of the long-wave band only, shows that the *p*H effect permits the following sequence for substituents on the 6-position

H	Cl	OH (4-acetic acid)	OH
−10 mμ	−4 mμ	16 mμ	26 mμ

5. In the case of isocytosine (2-amino-6-hydroxypyrimidine) the greatest shift of the long-wave maximum occurs between *p*H 4 and the *p*H range 5–8; while at *p*H 9.0 there is a sudden shift of this band to an intermediate position. Furthermore, this new position is midway between the two subsidiary peaks as shown at *p*H 5.0.

6. A consideration of the lower of the two subsidiary peaks (264 mμ) together with the peaks at *p*H 4 and 9 shows that the shift from *p*H 4 to *p*H 5 is 6 mμ and from *p*H 5 to *p*H 9, 12 mμ. These same values are obtained from the data of isocytosine-4-acetic acid.

TABLE IV

Compound	Long wave band λ_{max}, mμ	Long wave band Molar absorb. index	Short wave band λ_{max}, mμ	Short wave band Molar absorb. index	*p*H	
2-Chloro-6-aminopyrimidine	250	10600	...	...	3.0	
	272	5000	232	8500	7.0	
	272	5000	232	8500	11.0	
Cytosine	275	10200	...	...	0.1	*N* HCl
	274	9600	...	...	4.0	
	268	7550	227	5000	5.0	
	266	6600	...	...	7.4	
	266	5400	...	...	9.0	
	278	6800	...	...	11.0	
2-Methyl-4-hydroxy-6-ethoxypyrimidine	256	3600	227	9000	3.0	
	266	4500	...	...	7.0	
	266	3800	...	...	11.0	
2-Ethoxy-6-aminopyrimidine	268	4300	...	...	3.0	
	276	5000	224	11400	7.0	
	276	5000	224	11400	11.0	
2-Methyl-5-cyano-6-aminopyrimidine	293	4500	242	10000	3.0	
	293	4500	242	9000	7.0	
	280	3600	247	11000	0.1	*N* NaOH

Table IV includes the data for some unsymmetrical pyrimidines, none of which contains the 2 amino group. Examination shows that:

1. The spectrum of each compound shows two maxima for at least one *p*H value investigated.

2. The two peaks of the 2-hydroxy-6-aminopyrimidine (*p*H 5) are separated by the same amount as those of 2-chloro-6-aminopyrimidine (*p*H 7), although the latter are displaced 4 mμ toward longer wave lengths.

3. The position of λ_{max} shifts progressively toward shorter wave lengths in 2-hydroxy-6-amino pyrimidine (cytosine) when the *p*H is changed from 2 to 9, but at *p*H 11, λ_{max} occurs at a wave length longer than at *p*H 2.0. Thus in this particular compound the auxochromic character of the amino group appears only if *p*H 2 and 11 are considered.

4. In the case of the 2-chloro-6-aminopyrimidine the generally recognized characteristics of the amino group are evident (*cf.* 2-amino-6-chloropyrimidine).

5. The ratio of the positions of the short- and the long-wave maxima for 2-methyl-4-hydroxy-6 ethoxypyrimidine and the corresponding ratio for isocytosine shows that the relative separations and also $\Delta\lambda_{max}$ are similar, thus indicating a possible equality in the positional effect of the 4- and the 6-positions when occupied by the hydroxy group.

An over-all examination of the data reveals that, of the common auxochromes, the hydroxy group and the amino group both fail to produce the usual bathochromic effect when their introduction into the molecule results in a change from an unsymmetrical to a symmetrical molecule. This is illustrated by the following: (a) the introduction of the hydroxy group in uracil to give barbituric acid; (b) the introduction of the amino group into cytosine to give 4,6-diamino-2-hydroxypyrimidine.

The resulting symmetrical compounds do not show a shift of λ_{max} with *p*H and, further, show their principal absorption maximum at slightly shorter, rather than at longer, wave lengths than do the theoretical parent compounds.

Experimental

Materials.—Barbituric acid (Eastman Kodak Co.) was thrice precipitated from aqueous alcohol and was used as a 0.0000528 *M* solution, at *p*H 3, 7, 11. The molar absorbancy index agrees substantially with that given by Heyroth and Loofbourow[8] and Loofbourow and Stimson.[4] The 2-thio-4,6-dihydroxy-5-ethylpyrimidine and 2-methyl-4-hydroxy-6-ethoxypyrimidine were obtained through the courtesy of Merck & Co., and the first of these was used in 0.0000465 *M* solution at *p*H 4, 7.4, 11. The latter was employed in 0.000246 *M* solution at *p*H 3, 7, 11.

4,6-Dihydroxypyrimidine was prepared according to Kenner, *et al.*[9] It was employed in a 0.0000156 *M* solution at *p*H 2.9, 7, 10.9.

2-Hydroxy-4,6-diaminopyrimidine was prepared according to Todd[10] and employed in a 0.0000317 *M* solution at *p*H 2.7, 7.2, 10.9.

The 2-hydroxy-4,5,6-triaminopyrimidine was prepared according to Wieland and Liebig[11] and was measured in a 0.000124 *M* solution at *p*H 2, 2.5, 3.3, 6.4, 7.4, 10, 11.

2-Thio-4,6-diaminopyrimidine, prepared according to Traube,[12] was employed as a 0.0000704 *M* solution in 0.1 *N* hydrochloric acid, and at *p*H 2.2, 3.6, 4.4, 5.2, 5.4, 7.4, 9, 11. All the di- and triamino derivatives were kept in subdued light between the time the solution was prepared and the spectra determined to prevent formation of any colored oxidation compound.[13]

Uracil was employed in a 0.0000142 *M* solution at *p*H

(8) Heyroth and Loofbourow, THIS JOURNAL, **56**, 1728 (1934).

(9) Kenner, Lythgoe, Todd and Topham, *J. Chem. Soc.*, 388 (1943).

(10) A. R. Todd, personal communication.

(11) Wieland and Liebig, *Ann.*, **555**, 146 (1943).

(12) Traube, *ibid.*, **331**, 64 (1904).

(13) Polonovski, Vieillefosse, Guinand and Jerome, *Bull. soc. chim.*, 80 (1946).

3, 7, 11. Thymine was prepared by Dr. Marian Van Ess of the Golden State Co., and was measured in a 0.000193 *M* solution at *p*H 3, 7, 11. 5-Amino- and 5-nitrouracil (Eastman) were purified by repeated precipitation from aqueous solution and were measured in 0.000238 *M* and 0.000112 *M* solutions, respectively, at *p*H 3, 7, 11.

Isobarbituric acid was obtained from Dr. F. F. Heyroth of the University of Cincinnati and was measured in a 0.0002 *M* solution at *p*H 4, 7.4, 11. 5-Carboxyuracil was prepared by Dr. Elizabeth Ballard and is the material reported by her.[14]

2-Aminopyrimidine was obtained through the courtesy of Dr. R. O. Roblin of the American Cyanamid Co., and was measured in a 0.000165 *M* solution at *p*H 3, 7, 11. 2-Amino-6-chloropyrimidine (m. p. 178–179°) and its isomer (m. p. 209–210°) were employed in 0.000325 and 0.000232 *M* solutions, respectively, at *p*H 3, 7, 11.

Isocytosine monohydrate[15] (m. p. 275°) was used in a 0.0001185 *M* solution at *p*H 4, 5, 5.4, 6.4, 7.2, 7.4, 8, 9. Isocytosine-4-acetic acid was prepared by the late Dr. David E. Worrall and was described by him.[16] It was measured at *p*H 3, 7, 11 in a 0.000115 *M* solution.

Cytosine monohydrate was prepared by the method of Hilbert and Johnson[17] and was measured in a 0.000031 *M* solution at 0.1 *N* hydrochloric acid, *p*H 4, 5, 7.4, 9, 11.

(14) Ballard and Johnson, THIS JOURNAL, **64**, 794 (1942).
(15) Caldwell and Kline, *ibid.*, **62**, 2365 (1940).
(16) Worrall, *ibid.*, **65**, 2053 (1943).
(17) Hilbert and Johnson, *ibid.*, **52**, 1152 (1930).

The 2-ethoxy-6-aminopyrimidine was obtained from the American Cyanamid Co., and was used in a 0.000103 *M* solution at *p*H 3, 7, 11. 2-Methyl-5-cyano-6-aminopyrimidine (m. p. 243–244°) was employed in a 0.000223 *M* solution with 0.1 *N* hydrochloric acid, 0.1 *N* sodium hydroxide and *p*H 7.4.

Except for the listed cases where either hydrochloric acid or sodium hydroxide were used all *p*H values were obtained with Kolthoff buffer tablets. In every case the comparison cells were filled with corresponding buffer, acid or base.

Summary

1. In the pyrimidines investigated, which have a plane of symmetry through the 2–5 positions, there is essentially no change in the position of λ_{max} with change in *p*H.

2. 5-Uracil derivatives show an increase in λ_{max} which may be related to the dipole moment of the substituent.

3. When the introduction of an auxochrome produces a symmetrical structure the introduction is not accompanied by the bathochromic shift usually met.

CINCINNATI, OHIO
ADRIAN, MICHIGAN

RECEIVED JULY 26, 1948

[CONTRIBUTION FROM MELLON INSTITUTE AND DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Acetoxymethyl and Hydroxymethyldisiloxanes

BY JOHN L. SPEIER, B. F. DAUBERT AND R. R. MCGREGOR

As a continuation of the study of hydroxymethylsilicon compounds first reported by Speier, *et al.*,[1] who prepared trimethylsilylmethanol and studied its reactivity, acetoxymethyl and hydroxymethyldisiloxanes have been synthesized. The esters, acetoxymethylpentamethyldisiloxane and *sym.* bis-acetoxymethyltetramethyldisiloxane were prepared and from the latter *sym*-bis-hydroxymethyltetramethyldisiloxane was made by alcoholysis. The di-alcohol was found to be unstable, even at room temperature, but it could be handled, and a derivative was made with no noteworthy difficulty.

Experimental

Preparation of Acetoxymethyldisiloxanes.—Chloromethylpentamethyldisiloxane[2,3] was heated to reflux gently for twenty-four hours with a slight excess of anhydrous potassium acetate in a volume of glacial acetic acid equal to that of the disiloxane. The chloromethyl compound was not noticeably soluble in the mixture, but dissolved after several hours as a large amount of potassium chloride precipitated. The mixture was finally washed thoroughly with distilled water, and the water insoluble material was distilled. Very nearly the following molar proportions of products resulted: hexamethyldisiloxane[4] 25 mole %, b. p. 98–99° at 735 mm., $n^{25}D$ 1.3748; acetoxymethylpentamethyldisiloxane, 50 mole %, b. p. 180 at 735 mm., $n^{25}D$ 1.4040, d^{25}_4 0.902. *Anal.* Calcd. for $AcOCH_2SiMe_2OSiMe_3$: Si, 25.5; sapn. equiv., 220; molar refr.,[5] 59.82. Found: Si, 25.4; sapn. equiv., 219, 221; molar refr., 59.84; and *sym*-bis-acetoxymethyltetramethyldisiloxane, 25 mole %, b. p. 250° at 730 mm., $n^{25}D$ 1.4215, d^{25}_4 0.993. *Anal.* Calcd. for $(AcOCH_2Me_2Si)_2O$: Si, 21.2; sapn. quiv., 139.2; molar refr., 71.42. Found: Si, 21.1; sapn. equiv., 142, 141; molar refr., 71.2.

When *sym*-bis-chloromethyltetramethyldisiloxane was similarly treated, a practically quantitative yield of this product resulted.

Cleavage of Acetoxymethyldisiloxanes.—Both acetoxymethylpentamethyldisiloxane and *sym*-bis-acetoxymethyltetramethyldisiloxane were found to be resistant to acid hydrolysis. Neither ester was hydrolyzed to any appreciable extent after refluxing as long as 56 hours with 6 *N* sulfuric acid.

Both esters undergo rapid decomposition when treated with aqueous alkali. Cleavage of the Si–C bond occurred with the formation of methyl acetate and polysiloxanes. In one typical experiment, the diacetate ester was added quickly to boiling 2 *N* sodium hydroxide solution in 50% ethanol under a one-foot Vigreux column. Methyl acetate was distilled from the mixture as quickly as possible to minimize its saponification by the alkali. Two low boiling fractions were obtained: I, b. p. 53–58, $n^{25}D$ 1.3551 had the odor of methyl acetate; sapn. equiv., calcd. 74; found, 78. This was the chief product. II, b. p. 58–67°, $n^{25}D$ 1.3361, yielded a 3,5-dinitrobenzoate, m. p. 106–107° and is thus identified as being largely methanol, b. p. 66°, $n^{25}D$ 1.3276, 3,5-dinitrobenzoate, m. p. 107°. This fraction also contained methyl acetate, judging by its odor and by the fact that it contained saponifiable material. When the distillate rose to a b. p. of 100°, the residue was cooled, acidified and extracted with benzene. The extract was distilled through the Vigreux column. Most of the silicon-containing product was obtained at 135–142°,

(1) Speier, Daubert and McGregor, THIS JOURNAL, **70**, 117 (1948).
(2) Krieble and Elliott, *ibid.*, **67**, 1810 (1945).
(3) Bluestein, *ibid.*, **70**, 3068 (1948).
(4) Hunter, Warrick, Hyde and Curry, *ibid.*, **68**, 2284 (1946).
(5) Warrick, *ibid.*, **68**, 2455 (1946).