less pseudo-bases on hydrolysis of several benzopyrylium salts by previous investigators[5] also supports the above results.

TABLE I

THE EQUILIBRIUM BETWEEN HYDRONIUM IONS, AND THE BENZOPYRYLIUM SALT AND THE PSEUDO-BASE OF PELARGONIDIN 3-MONOGLUCOSIDE AT 25°

*p*H	Optical density at 500 mμ	R$^+$, %	*pK*
1.18	1.075	98.4	2.99
1.42	1.050	96.2	2.82
1.74	1.025	93.7	2.92
1.99	0.980	89.7	2.93
2.16	.928	85.0	2.91
2.49	.855	78.3	3.05
2.58	.775	71.0	2.97
2.77	.665	60.9	2.96
3.08	.490	44.9	2.99
3.36	.338	30.9	3.01
3.62	.227	20.8	3.04
3.83	.159	14.6	3.06
4.01	.118	10.8	3.09
		Av. *pK*	2.98 ± 0.06

The anthocyanin was isolated from strawberries by a previously described method.[2] It was purified by recrystallizing the picrate six times and then converted to the chloride. The values in Table I were obtained with a 4.27×10^{-5} molar anthocyanin solution in Sörensen's disodium citrate–hydrochloric acid buffers. Measurements were taken at 500 mμ with a Beckman spectrophotometer, model C, using 1 cm. Corex cells, at least one hour after the solutions had been prepared. The *p*H values were determined with a Beckman *p*H meter, model G. All measurements were made at 25°.

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(5) P. Karrer and C. Trugenberger, *Helv. Chim. Acta*, **28**, 444 (1945); I. M. Heilbron and A. Zaki, *J. Chem. Soc.* 1902 (1926); D. W. Hill and R. R. Melhuish, *ibid.*, 1161 (1935).

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A New Synthesis of Oxindole

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While evaluating known[1,2] and potential methods for preparing oxindole, it was found that the synthesis used by Meyer and Beer[3] to prepare 3,4-dihydrocarbostyril from 2-chlorodihydrocinnamic acid could also be used for the synthesis of oxindole. The method consisted of heating *o*-chlorophenylacetic acid with concentrated ammonium hydroxide and copper powder in a sealed tube at 155–165° for eight hours whereupon cyclization to form oxindole took place.

Experimental

***o*-Chlorobenzyl cyanide** was prepared in a 91–94% yield from *o*-chlorobenzyl chloride by a method similar to that given in "Organic Syntheses" for the preparation of benzyl cyanide.[4]

***o*-Chlorophenylacetic acid** was prepared in an 85–88% yield from *o*-chlorobenzyl cyanide by a method similar to that given in "Organic Syntheses" for the preparation of phenylacetic acid.[5]

Oxindole.—The best yields of oxindole were obtained by using the following conditions. A mixture of 5.3 g. (0.031 mole) of *o*-chlorophenylacetic acid, 0.56 g. of copper powder or 1.0 g. of cupric acetate and 28 ml. of concd. ammonium hydroxide was heated in a sealed pressure tube at 155–165° for 8 hours in a Carius oven. After allowing the tube to come to room temperature in the oven, the tube was opened, and the crystals which formed were filtered, dissolved in hot water and treated with Darco. On cooling, the white crystals which formed were filtered and dried. A yield of 1.4 to 1.8 g. (34 to 43%) of oxindole melting at 126–127° was obtained. A mixed melting point of this compound with an authentic sample of oxindole prepared by the method of Di Carlo[6] showed no depression.

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(1) See W. C. Sumpter, *Chem. Revs.*, **37**, 443 (1945), for a review of the methods for preparing oxindole.

(2) At the time that this work was begun the method by which R. Stolle and R. Bergdoll, *J. prakt. Chem.*, **128**, 1 (1930), cyclized α-chloroacetanilide with aluminium chloride was found to be unsuccessful. Subsequently the work of S. Sugassawa, I. Satoda and J. Yanagisawa, *J. Pharm. Soc. Japan*, **58**, 139 (In English 29) (1938), showed that a ratio of 1.8 parts of aluminum chloride to one part of α-choloroacetanilide was necessary for the reaction instead of a ratio of one to one as reported by Stolle and Bergdoll. Similar results have been reported recently by P. L. Julian in "Heterocyclic Compounds," Vol. 3, R. C. Elderfield, ed., John Wiley and Sons, Inc., New York, N. Y., 1952, p. 144.

(3) H. Meyer and R. Beer, *Monatsh.*, **34**, 1179 (1913).

(4) R. Adams and A. F. Thal, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 107.

(5) Reference 4, p. 437, note 3.

(6) F. J. Di Carlo, THIS JOURNAL, **66**, 1420 (1944).

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Urea–Formaldehyde Kinetic Studies. IV. Reactions of Methylenebisureas

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In the course of studies of the reaction of dilute solutions of urea and simple N-alkylureas with formaldehyde at *p*H 7.15 it was observed that certain methylenebisureas once formed, showed no sign of hydrolysis, further condensation or polymerization.[1] Methylene compounds have been postulated as important units in urea–formaldehyde plastics and it was desirable that the reactions of methylenebisureas be studied further. It was found that the polarographic method of analysis used previously[1] was more suitable for this study than titration methods. The use of titration methods for the estimation of formaldehyde when working with more concentrated solutions must receive careful consideration, since condensation products have been shown to influence the estimation.[2] Preliminary studies have indicated that methylol compounds,[2] methylenebisureas and more highly condensed systems each have separately different effects on the usual titration methods. Consequently, the study of later stages of condensation in more concentrated solution must await reliable analytical methods. Borzee and Smetz[3] have recently used titration methods in a study of condensation reactions of urea and formaldehyde in concentrated solution but do not state whether errors were introduced by the condensation products.

The present work concerning the formation[1] and reactions of methylenebisureas requires further

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(1) L. E. Smythe, THIS JOURNAL, **75**, 574 (1953).

(2) L. E. Smythe, *J. Phys. Colloid Chem.*, **51**, 396 (1947).