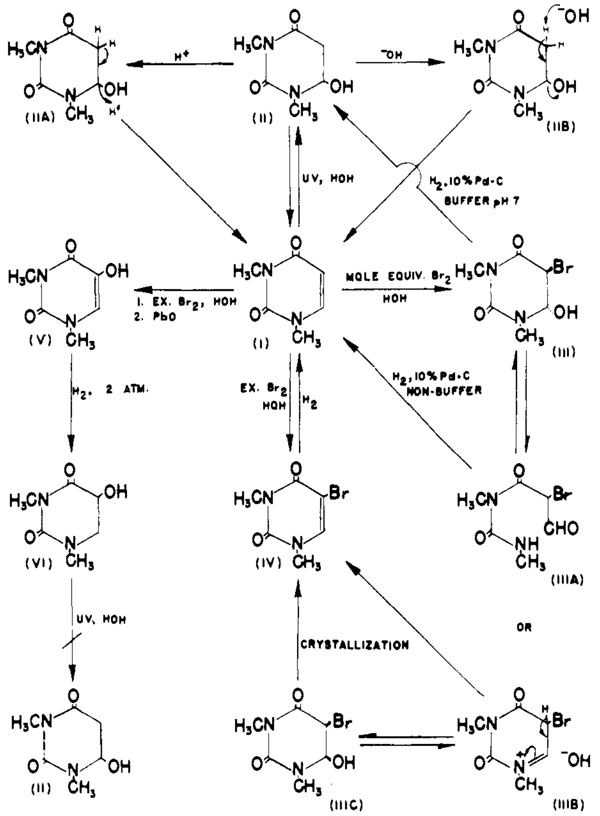
ULTRAVIOLET IRRADIATION OF 1,3-DIMETHYLURACIL[1]

Sir:

1,3-Dimethyluracil (I)[2] was used to study the interesting but poorly understood ultraviolet irradiation effects on nucleic acids.[3] (I) (m.p. 121–122°; $\lambda_{max}^{H_2O}$ 267 mμ, ε 8.67 × 10³: $\lambda_{min}^{H_2O}$ 235 mμ, ε 1.68 × 10³; λ250/λ260, λ280/λ260; 0.62, 0.62 for *p*H 2–12; ν_{CO}^{KCl} 1701 cm⁻¹) in aqueous solution (0.067*M*) was irradiated with ultraviolet light until 80–90% of the optical density at 260 mμ had disappeared. The irradiated product (60–75% yield) was recrystallized from chloroform and petroleum ether and gave 6-hydroxy-1,3-dimethylhydrouracil (II),[4] m.p. 105–106° (found: C, 45.61; H, 6.49; N, 18.00; ν_{OH}^{KCl} 3344 cm.⁻¹, ν_{CO}^{KCl} 1704 cm.⁻¹). On treating (II) with acid (*p*H 2), alkali (*p*H 9, 10, 11, 12) or heat, respectively, the ultraviolet spectrum of (I) was reconstituted (λ250/λ260, λ280/λ260; 0.62, 0.62; 0.61, 0.62; 0.60, 0.62; 0.62, 0.63; 0.61, 0.62). Over 90% yield of (I) was obtained in the acidic and alkaline reconstitutions.



On treating (I) with an excess of bromine water, 5-bromo-1,3-dimethyluracil (IV), m.p. 184–185°, was obtained (found: C, 33.03; H, 3.40; N, 12.66; Br, 36.20; $\lambda_{max}^{H_2O}$ 283 mμ, ε 8.57 × 10³; $\lambda_{min}^{H_2O}$ 246 mμ, ε 1.57 × 10³; ν_{CO}^{KCl} 1684 cm.⁻¹). When (I) was treated with excess bromine water, followed by boiling with lead oxide, 5-hydroxy-1,3-dimethyluracil (V) m.p. 198–199° (found: C, 46.15; H, 5.38; N, 17.83; $\lambda_{max}^{H_2O}$ 285 mμ, ε 7.35 × 10³; $\lambda_{min}^{H_2O}$ 248 mμ, ε 1.78 × 10³; ν_{OH}^{KCl} 3215 cm.⁻¹, ν_{CO}^{KCl} 1669 cm.⁻¹) was obtained. Hydrogenation of (V) at two atmospheric pressures gave 5-hydroxy-1,3-dimethylhydrouracil (VI), m.p. 109–110° (found: C, 45.57; H, 6.40; N, 17.92; ν_{OH}^{KCl} 3390 cm.⁻¹, ν_{CO}^{KCl} 1704 cm.⁻¹). No reconstitution of (VI) under similar conditions. When (VI) was irradiated, then treated with acid or alkali, there was no change in ultraviolet spectrum, indicating that (VI) was not converted to (II) on irradiation. These observations suggested strongly that (VI) was not an intermediate.

When (I) was treated with one mole equivalent of bromine water *trans* 5-bromo-6-hydroxy-1,3-dimethylhydrouracil (III) was obtained in solution. There was no detectable change in ultraviolet spectrum after standing for two hours. However, when the solution was allowed to stand overnight or crystallized from the $CHCl_3$ extract, only (IV) was obtained. This dehydration probably went by way of the "mutarotation" (IIIA) or (IIIB). Hydrogenolysis of (III) in a non-buffered solution gave only (I) as the product. However, hydrogenolysis of (III) in a phosphate buffered solution, *p*H 7, gave (II), m.p. 105–106° in over 50% yield. This was identical with the irradiated product as determined by m.m.p. 105–106°, infrared and analysis (found: C, 45.56; H, 6.49; N, 17.71). (II) was thus identified by synthesis as 6-hydroxy-1,3-dimethylhydrouracil, suggesting a 1,4-addition as the mechanism of the photo-reaction.

The kinetics of the photo-addition were zero order as shown by a plot of optical density *vs.* time. The acid catalyzed dehydration (*p*H 1.98) (IIA), and the base catalyzed β-elimination (*p*H 9.01) (IIB) were both of the first order as shown by a plot of log C_0/C_t *vs.* time.

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[2] A. M. Moore and C. H. Thomson, *Science*, **122**, 594 (1955), and references therein.

[3] E. Chargaff and J. N. Davidson, "The Nucleic Acids," Vol. I, p. 123, Academic Press, Inc., New York, N. Y.

[4] The product of Moore and Thomson, m.p. 102°. Following the nomenclature used in *Chemical Abstracts* (II) should be called 1,3-dimethyl-5,6-dihydro-6-hydroxy-2,4-pyrimidinedione.

THE BASIC RING SYSTEM OF CRININE

Sir:

Two recent communications have suggested the likelihood that several alkaloids of the *Amaryllidaceae* possess structures containing a spiro ring system.[1,2] The following results establish a new spiro ring system for crinine.[3]

Manganese dioxide oxidation of crinine, $C_{15}H_{14}N(O_2CH_2)(OH)$, m.p. 210°, gave an α,β-unsaturated ketone, oxocrinine (m.p. 183–185°; found: C, 71.15; H, 5.52; N, 5.21; $\lambda_{max}^{CHCl_3}$ 5.98 μ; λ_{max}^{EtOH} 227 mμ (4.20), 296 mμ (3.59)). Lithium aluminum hydride reduction of oxocrinine afforded *epi*crinine

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[1] S. Kobayashi, T. Shingu and S. Uyeo, *Chemistry and Industry* 177 (1956).

[2] T. Ikeda, W. I. Taylor, Y. Tsuda and S. Uyeo, *ibid.*, p. 411.

[3] Crinine was reported by L. H. Mason, E. R. Puschett and W. C. Wildman, THIS JOURNAL, **77**, 1253 (1955); in *Chem. Ber.*, **87**, 1704 (1954), H.-G. Boit reported the same alkaloid as "crinidine."