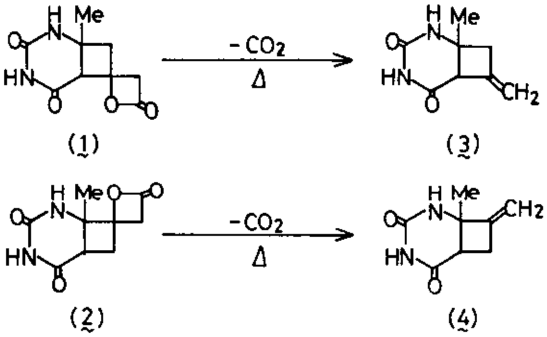
STUDIES ON KETENE AND ITS DERIVATIVES (CVIII).[1] PHOTOREACTION OF DIKETENE WITH URACIL (COMPLEMENT)

Takuo Chiba, Hitoshi Takahashi, and Tetsuzo Kato*

Pharmaceutical Institute, Tohoku University, Aobayama, Sendai 980, Japan

Abstract —— Photoreaction of diketene with uracil gave the [2+2]spiro-cycloadduct, which was, on thermolysis, transformed to 7- and 8-methylene-2,4-diazabicyclo[4.2.0]octane-3,5-dione (5) and (6). Bromination of compound (5) followed by the treatment with sodium ethoxide gave 5-methylene-5,6-dihydro-1*H*,3*H*-cyclobuta[e]pyrimidine-2,4-dione (7).

Previously, we have reported the photoreaction of diketene with 6-methyluracil to give [2+2 – 4]-spiro-cycloadducts such as (1) and (2), which, on heating, were transformed to the di-azabicyclo[4.2.0]octane derivatives such as (3) and (4).[1] In the present report we wish to describe the continuation of this study on the reaction with uracil.



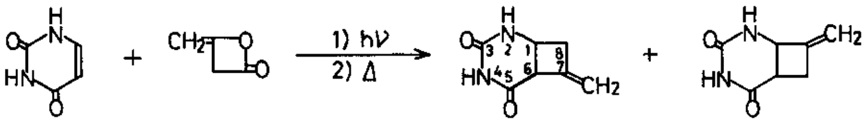
(1) (3)

(2) (4)

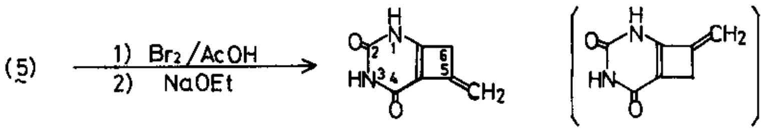
A solution of uracil (5.6 g, 0.05 mol) and diketene (42 g, 0.5 mol) in aq. acetone (50%) was irradiated with a high pressure mercury lamp (400 W) for 6 h. After removal of the solvent and excess diketene, the reaction mixture (10.5 g, $\nu_{max.}$ (KBr) 1 840 cm^{-1}) was heated at 220 °C for 20 min. Purification by silica gel column chromatography using ethyl acetate as an eluent afforded a mixture (3 : 1) of 7- and 8-methylene-2,4-diazabicyclo[4.2.0]octane-3,5-dione (5) and (6), 3.16 g (42%). Recrystallization from methanol gave compound (5), m.p. 213 – 215 °C, colorless prisms [Found: C, 55.15; H, 5.3; N, 18.4. $C_7H_8N_2O_2$ requires C, 55.25; H, 5.3; N, 18.4%; $\nu_{max.}$ (KBr) 3 230, 3 060, 1 705, and 1 685 cm^{-1}; δ (CF_3CO_2H) 2.90 – 3.43 (2H, m, C_8-H), 3.43 – 3.83 (1H, m, C_6-H), 4.53 – 4.97 (1H, m, C_1-H), 5.00 – 5.30 (2H, m, *exo*-methylene), 7.50

- 7.90 (1H, br, N_2-H), and 9.03 - 9.60 (1H, br, N_4-H)] and compound (6), m.p. 238 °C, colorless needles [Found: C, 55.2; H, 5.3; N, 18.4. $C_7H_8N_2O_2$ requires C, 55.25; H, 5.3; N, 18.4%; $\nu_{max.}$ (KBr) 3 200, 3 070, 1 720, and 1 660 cm^{-1}; δ (CF_3CO_2H) 2.90 - 3.33 (2H, m, C_7-H), 4.00 - 4.57 (2H, m, C_1-H, C_6-H), 4.97 - 5.43 (2H, m, *exo*-methylene), 7.27 - 7.70 (1H, br, N_2-H), and 9.10 - 9.63 (1H, br, N_4-H)]. Structures of (5) and (6) were established by comparison of NMR spectral data for cycloadducts derived from uracil and isobutylene.[2]

A mixture of (5) and (6) (1.52 g, 3 : 1 ratio) was dissolved in acetic acid (30 ml). To this solution was added dropwise a solution of bromine (1.6 g) in acetic acid (5 ml). The mixture was distilled, and the resulting residue was recrystallized from ethanol to give a crystalline substance, 2.08 g, a part of which (0.62 g) was treated with sodium ethoxide prepared from sodium (0.09 g) and absolute ethanol (10 ml) to give 0.1 g of 5-methylene-5,6-dihydro-1*H*,3*H*-cyclobuta[e]pyrimidine-2,4-dione (7), m.p. 234 °C (decomp.), as colorless needles [$\nu_{max.}$ (KBr) 3 210, 3 000, 1 730, and 1 665 cm^{-1}; δ (CF_3CO_2H) 3.56 (2H, s, C_6-H), 5.58 (1H, d, *J* 2 Hz, *exo*-methylene), 5.78 (1H, d, *J* 2 Hz, *exo*-methylene), 7.40 - 7.73 (1H, br, N_2-H), and 9.77 - 10.20 (1H, br, N_4-H); *m*/e 151 (*M*+1)]. The structure of 7 was determined by a spin-spin decoupling for N_1 protons and C_6-methylene protons. In this reaction the 6-methylene derivative (8) derived from (6) could not be detected.



(5) (6)



(7) (8)

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