Photochemical Formation and Some Chemical Properties of 2,6-Diazabicyclo[2.2.0]hexane-3,5-diones from Pyrimidinium-4-olates. A New Approach to Novel Bis(β lactams)

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The pyrimidinium-4-olates of type (1) or (3) are photochemically isomerized into the novel bis(β -lactams) (2) or (4), respectively, and the bis(β -lactam) (2a) could be further converted into two monocyclic β -lactams.

In connection with our work on 1,4-dipolar cycloaddition reactions of pyrimidinium-4-olates of type $(1)^1$ to alkynes,² NN double bonds,³ carbonyl compounds, and ketenes,⁴ as well as to singlet oxygen,⁵ we have now studied the photochemical behaviour of this interesting class of compounds. Herein we report the photochemical isomerization of pyrimidinium-4-olates which offers a new approach to novel bis(β lactams) of type (2) and (4), as well as some thermal reactions of (2).

After 3,6-dihydro-6-oxo-1,3-diphenyl-1-pyrimidinium-4olate³ (**1a**) had been irradiated with a medium-pressure mercury arc in acetonitrile at 20 °C, crystallization from ethyl acetate-hexane afforded a 96% yield of the colourless 2,6-diazabicyclo[2.2.0]hexane-3,5-dione derivative of type (**2a**), whose constitution was established by elemental analysis and spectroscopic data (Scheme 1, Table 1).

Similarly, irradiation of the pyrimidinium-4-olates (1b, c,³ d,⁶ e⁷) produced colourless crystals of the novel bis(β -lactams) (2b-e), respectively (Scheme 1, Table 1).[†] Also the bicyclic pyrimidinium-4-olates (3a,b)[‡] underwent photochemical isomerization with formation of the new tricyclic bis(β lactams) of type (4a) or (4b), respectively (Scheme 1, Table 1).[†]

Since the signs of the highest SOMO coefficients at positions 2 and 5 of the pyrimidinium-4-olates are equal, the observed isomerizations of (1) to (2) or (3) to (4) are, according to the rules of conservation of orbital symmetry,⁸ results of a photochemically allowed, disrotatory electrocyclic ring closure of electronically excited (1) or (3), respectively.

On heating at 235 °C, (2a) was converted back into (1a), whereas in the presence of 2,4,6-trichlorophenol, the β -lactam derivative (8) was formed in 12% yield, m.p. 188–189 °C (Scheme 2).†

Table 1. 2,6-Diazabicyclo[2.2.0]hexane-3,5-diones (2) and (4) from (1) or (3).

(1), (2)	R۱	\mathbb{R}^2	R ³	% Yield	M.p. (t/°C)
а	Ph	Н	Ph	96	189
b	Ph	Me	Н	91	146147
с	Ph	Me	Me	83	147—148
d	Ph	Me	Ph	61	200.5-201.5ª
e	Me	SEt	Ph	92	135.5-136.5ª
(4a)				64	123.5-124
(4 b)				92	144145

^a Decomp.

Treatment of (2a) with zinc chloride in boiling methanol for 2 days produced a 69% yield of the phenylmalonic acid derivative (5). However, after refluxing of (2a) for 15 min in methanol in the presence of a catalytic amount of sodium methoxide, the new β -lactam (9), (6%)† as well as the known compounds (10) (26%) and (11) (62%) were generated as



[†] All new compounds gave satisfactory microanalytical data and their spectroscopic properties were as expected.

 $[\]ddagger$ Synthesis in accordance with the procedure of ref. 3, (3a), m.p. 254-255 °C (decomp.), yield 75%; (3b), m.p. 290-292 °C (decomp.), yield 80%.

outlined in Scheme 2. The *trans*-configuration of (9) was established from the magnitude of the vicinal ${}^{1}H{-}{}^{1}H$ coupling constant (J 2.3 Hz) in the ${}^{1}H$ n.m.r. spectrum which lies in the expected region of 2.2–2.8 Hz.^{9,10}

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