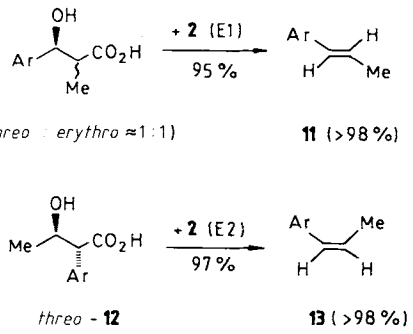
is connected with the (*Z*)-geometry[11]. **11** and **13** cannot be prepared in isomerically pure form by Wittig reaction[12], and they are almost unseparable even by TLC.



Scheme 2. Ar = 2,4,5-trimethylphenyl.

As an easy access to **11** and **13** we chose the reaction of **10** and **12** with **2** (Scheme 2). The electron-rich aryl group (R^2) in **10** enforces the E1 elimination and, quite consistently, **11** is formed from **10** in >98% yield. In the case of **12**, on the other hand, the methyl group induces an E2-mechanism; up to >98% of **13** is isolated. The transition from **10** to **12** corresponds to an interchange of substituents R^1 and R^2 with largely differing +M effects. The character of elimination is—in complete agreement with our interpretation—thereby completely shifted from E1 to E2.

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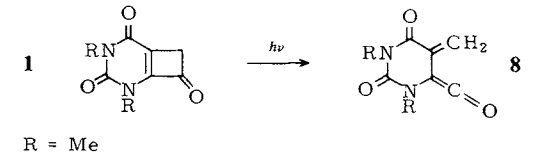
[7b] J. Mulzer, A. Pointner, A. Chucholowski, G. Brüntrup, *J. Chem. Soc. Chem. Commun. 1979*, 52.
[8] (Abstract) The use of *threo-erythro* descriptors for β-hydroxycarbonyl compounds is contradictory to the original convention derived from threose and erythrose. However, since more recent alternative descriptors do likewise not offer an ideal solution to the problem we stay by *threo-erythro* and—despite all reservations—define these configurations according to C. H. Heathcock, C. T. White, J. J. Mirrison, D. VanDerveer, *J. Org. Chem. 46* (1981) 1296.
[11] B. P. Saxena, O. Koul, K. Tikku, C. K. Atal, *Nature 270* (1977) 512.
[12] *Chem. Eng. News 1979*, April 16, p. 24.

Photocycloaddition of 6-Cyanouracil to Ketene Diethyl Acetal: Synthesis of a Uracil Derivative Possessing a Cyclobutenone Framework

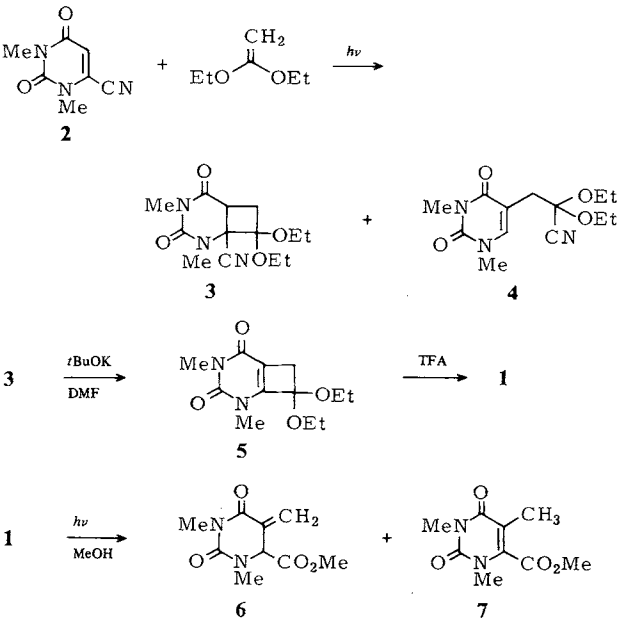
By *Isao Saito*, Fuyuhiko Kubota, Koji Shimozono,* and *Teruo Matsuura**

Dedicated to Professor G. O. Schenck on the occasion of his 70th birthday

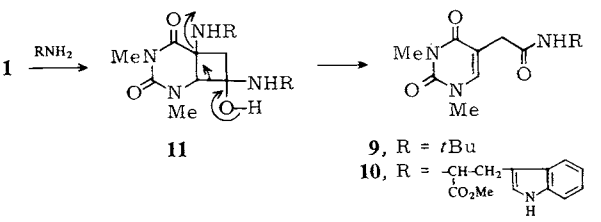
The synthesis of highly photochemically reactive pyrimidine bases is of special importance for photochemical modification of nucleic acids[1]. Upon irradiation, pyrimidine bases possessing cyclobutenone frameworks are expected to exhibit high reactivity toward nucleophiles, since photochemical ring-opening of cyclobutenone may produce highly reactive vinylketene derivatives[2]. We describe here the synthesis of 2,4-diazabicyclo[4.2.0]oct-1(6)-en-3,5,8-trione **1**, the first uracil derivative possessing a cyclobutenone framework, utilizing photocycloaddition as a key step.



Irradiation of 6-cyano-1,3-dimethyluracil, **2**, and excess ketene diethyl acetal in acetonitrile at −25 °C using a high-pressure mercury lamp (Pyrex filter) gave cycloadduct **3** (40%) and rearranged product **4** (23%). The formation of rearranged adducts such as **4** has previously been shown to occur in the photoaddition of **2** to other olefins[4]. Conversion of **3** into **5** (80%) was readily accomplished by reaction with potassium *t*-butoxide in dimethylformamide. Treatment of acetal **5** with 90% trifluoroacetic acid (TFA) gave cyclobutenone **1** (77%) [m.p. = 108–110 °C; ^{1}H-NMR ($CDCl_3$): δ = 3.38 (s, 3H), 3.40 (s, 3H), 3.67 (s, 2H)].



Cyclobutenone **1** is stable at ambient temperature in the usual organic solvents, including alcohols; however, irradiation of methanolic solutions of **1** resulted in rapid formation of **6** (55%) and **7** (21%). **7** also formed by prolonged irradiation of **6**, whereas the latter probably originates from the trapping of vinylketene **8** by methanol.



Unexpectedly, cyclobutenone **1** reacts smoothly with primary amines without irradiation at ambient temperature to give 5-substituted uracil derivatives in high yields. For example, treatment of **1** with *t*-butylamine gave **9** quantitatively. When a solution of **1** and tryptophan methyl ester

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in acetonitrile was stirred at room temperature, the adduct **10** precipitated (76%). Thus the cyclobutenone **1** can be used as a synthon for the preparation of 5-substituted uracil derivatives under neutral conditions. In view of the high reactivity of the CC double bond of cyclobutenones toward nucleophiles[2], **9** is assumed to arise from ring-opening of the amine adduct **11**[5].

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1, 86436-22-8; **2**, 49846-86-8; **3**, 86436-23-9; **4**, 86436-24-0; **5**, 86436-25-1; **6**, 85436-26-2; **7**, 83174-95-2; **9**, 86436-27-3; **10**, 86436-28-4; ketene diethyl acetal, 2678-54-8; tryptophan methyl ester, 4299-70-1.

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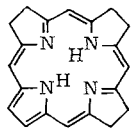
[2] R. Huisgen, H. Mayr, *J. Chem. Soc. Chem. Commun. 1976*, 55.
[4] I. Saito, K. Shimozono, T. Matsuura, *J. Am. Chem. Soc. 102* (1980) 3948; *ibid. 105* (1983) 936.
[5] For an analogous reaction, see A. Wexler, R. J. Balchunis, J. S. Swenton, *J. Chem. Soc. Chem. Commun. 1975*, 601.

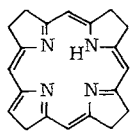
The Chemistry of Pyrrocorphins: Stereoselectivity in the Porphyrinogen→Pyrrocorphin Tautomerization**

By *Rudolf Waditschatka* and *Albert Eschenmoser**

As originally surmised[1], and recently demonstrated[2], the corphinoids play a central role in the biosynthesis of vitamin B_{12}. We report here new findings on the chemistry of the pyrrocorphins[3].



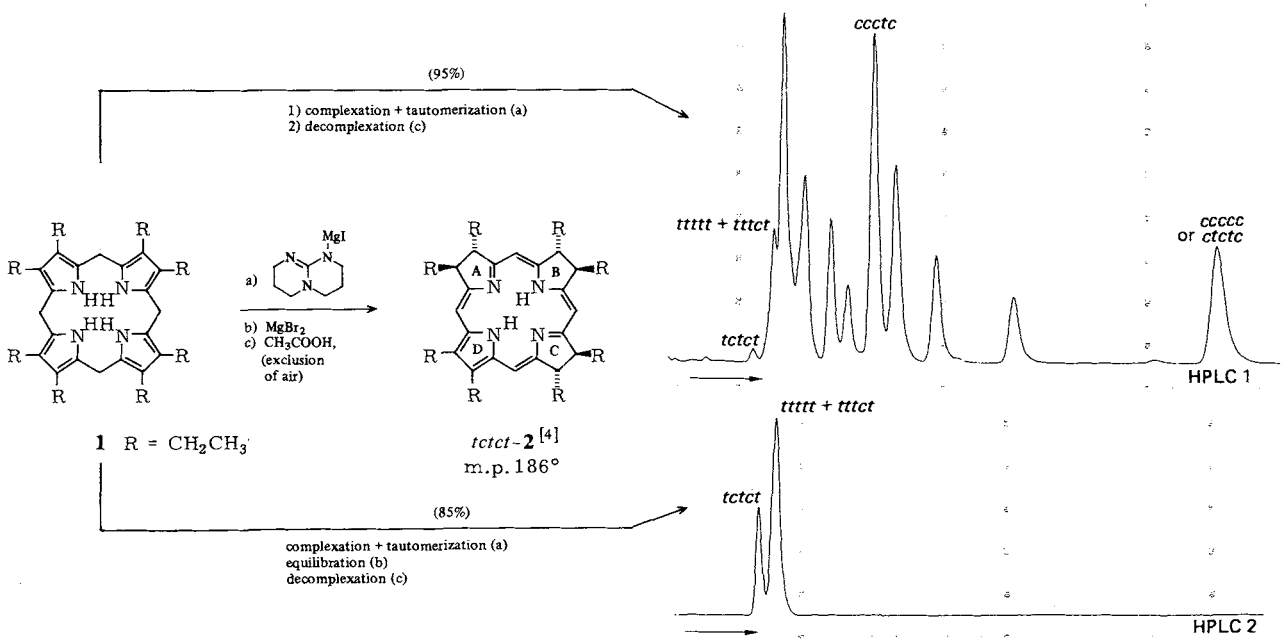
Pyrrocorphin[3]



Corphin[1]

Optimized reaction conditions have now been found for the previously reported[3a] porphyrinogen→pyrrocorphin tautomerization. Thus, treatment of octaethylporphyrinogen **1** with the MgI salt of 1,5,7-triazabicyclo[4.4.0]-dec-5-ene (TBD) directly followed by decomplexation with acetic acid (see legend to Scheme 1), provided a mixture of diastereomers of the octaethylpyrrocorphins **2** in practically quantitative yield. This endergonic isomerization proceeds *via* the non-isolated mixture of diastereomeric Mg pyrrocorphinate complexes (assumed to be decomplexed under conditions of kinetic control)[3a]. HPLC of the non-equilibrated mixture of pyrrocorphins resulted in detection of at least 12 of the 20 possible diastereomers (UV/VIS, HPLC 1), the configurations of three of which have been assigned. Normally, the *ccctc* isomer[3a,4] makes up the main part (15–20%) of such mixtures.

If the mixture is allowed to equilibrate between the tautomerization and the decomplexation steps, or the 12-component mixture is subjected to such conditions, a mixture of diastereomers is obtained in 85% yield, HPLC of which now shows only two fractions (HPLC 2). The first fraction (*ca.* 30% of the total mixture) is the readily crystallized



Scheme 1. R = Et. a) 8×10^{-3} M **1** in xylene, 15 equiv. TBD, 5 equiv. EtMgI, 16 h, 85°, under N_2. Work-up with saturated NaCl/H_2O (or c directly). b) 2×10^{-3} M Mg-complex of **2** in wet benzene, 12 equiv. $MgBr_2$, RT, 15 min. c) 10% CH_3COOH in saturated NaCl/H_2O, 1 min, *ca.* 20°C. All operations conducted in glove box (< 5 ppm O_2). HPLC Partisil 5; pentane + 1.5 vol.-% Et_3N, detection 340 nm. For experimental details see *R. Waditschatka*, Dissertation ETH Zürich (in preparation), and [5c].

isomer *tctct*-**2** (m.p. = 186°C). The second fraction is a binary (not crystallized) mixture of isomers *ttttt*-**2** (*ca.* 25%) and *tttct*-**2** (*ca.* 45%). Thus, *tctct*-**2**, a crystalline representative having the pyrrocorphin structure, can be prepared in 20–25% yield directly from octaethylporphyrinogen.

The configurational assignment of *tctct*-**2** rests on the complexation with nickel(II) acetate (acetic acid, 110°C, 5

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