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1,3,8,10,11,14-HEXAZAPENTAPHENE-2,4,7,9(14H,3H,8H,11H)-TETRAONES (BENT
DOUBLE-HEADED 5-DEAZAFLAVINS) WITH STRONG OXIDIZING POWER

Fumio Yoneda,^{*,a} Masakazu Koga,^a Toshiro Ibuka,^a and Yumihiko Yano^b

Faculty of Pharmaceutical Sciences, Kyoto University,^a Sakyo-ku, Kyoto 606, Japan
and Department of Chemistry, Gunma University,^b Kiryu, Gunma 376, Japan

1,3,8,10,11,14-Hexazapentaphene-2,4,7,9(14H,3H,8H,11H)-tetraones (bent double-headed 5-deazaflavins) were prepared by condensing N,N'-dialkyl-p-phenylenediamines and 6-chloro-5-formyl-3-methyluracil, and by cyclizing N,N'-dialkyl-N,N'-di(3-methyluracil-6-yl)-p-phenylenediamines with Vilsmeier reagent; these bent double-headed 5-deazaflavins oxidized alcohol under neutral condition in light and a remarked autorecycling occurred.

KEYWORDS — autorecycling oxidation; alcohol oxidation; Vilsmeier reagent; epoxidation; m-chloroperbenzoic acid; 5-deazaflavin; photosensitizer

Recently the flavin derivatives of extended conjugation, which consist of two flavins or two 5-deazaflavins with a benzo unit in common, have been synthesized.^{1,2)} A similar mixed system having both flavin and 5-deazaflavin was also synthesized.³⁾ As expected, these derivatives have high oxidizing activities toward alcohols.

We report here a novel class of extended conjugated compounds, 1,3,8,10,11,14-hexazapentaphene-2,4,7,9(14H,3H,8H,11H)-tetraones (**1**), which have a bent type structure and have strong oxidizing power. Compounds **1** were synthesized as follows (Method A). The starting N,N'-dialkyl-p-phenylenediamines (**2**) were prepared according to the known procedure.⁴⁾ Compounds **2** were condensed with two molar amounts of 6-chloro-5-formyl-3-methyluracil (**3**) in N,N'-dimethylformamide (DMF) for 5–9 h under reflux to give the corresponding **1** along with 10-alkyl-7-alkylamino-3-methyl-5-deazaflavins (**5**) (Chart 1).

Compounds **1** were synthesized alternatively as follows (Method B). Compounds **2** were treated with two molar amounts of 6-chloro-3-methyluracil (**6**) to give the corresponding N,N'-dialkyl-N,N'-di(3-methyluracil-6-yl)-p-phenylenediamines (**7**) according to the known procedure.²⁾ Treatment of **7** with Vilsmeier reagent (DMF-POCl₃) at 90°C for 5–6 h in argon atmosphere gave **1** in better yields than the above method (Chart 1).

In order to determine whether compounds **1** have a linear (**2**) or a bent form, we have carried out the epoxidation reaction of **1**.⁵⁾ Thus, **1a** was treated with m-chloroperbenzoic acid (MCPBA)⁶⁾ in chloroform for 3 h under reflux to give the corresponding epoxide (**8**)⁷⁾ in 18% yield, along with the recovered **1a** in 56% yield, after the chloroform solution was washed with aq Na₂S₂O₃, aq NaHCO₃ and water, dried,

should have strong oxidizing abilities. In fact, compounds **1** oxidized cyclopentanol to give cyclopentanone under neutral condition at 80°C in light and a remarked autorecycling occurred in the oxidation (Table II). During the reactions compounds **1** were gradually decomposed, and the decomposition products exhibited no further catalytic activity for the alcohol oxidation.

As reference compounds, photosensitizers such as methylene blue and Rose bengal, and also monomeric 5-deazaflavin, 3,10-dimethyl-5-deazaflavin,⁸⁾ were used for comparison with **1**. The photosensitizers did not catalyze the above alcohol oxidation at all under the same conditions. The 5-deazaflavin exhibited some oxidizing ability, although it was less effective than **1** (Table II).

Table II. Autorecycling Oxidation of cyclopentanol (1.5 ml) by **1** (0.5 mg) at 80°C for 25 h in Light (Sun Lamp DR 250/T(L), Toshiba; 10 cm Distance)

Compd.	Yield of cyclopentanone (%) ^{a)}	
1a	98,000 ^{b)}	6.8 ^{c)}
1b	120,000	6.2
1c	212,000	9.4
Methylene blue	0	0
Rose bengal	0	0
2,10-Dimethyl-5-deazaflavin	13,000	1.9

a) Isolated as the 2,4-dinitrophenylhydrazone.

b) Based on the catalysts.

c) Based on the starting cyclopentanol.

REFERENCES AND NOTES

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- 3) F. Yoneda, M. Koga, and T. Ibuka, *Tetrahedron Lett.*, 25, 5345 (1984).
- 4) P. Vouros and D. Biemann, *Org. Mass. Spectrom.*, 2, 375 (1969).
- 5) The structures of **1** could not be determined by direct NMR examinations because of their symmetry.
- 6) F. Yoneda and Y. Sakuma, *Tetrahedron Lett.*, 22, 3977 (1981).
- 7) The equivalent signals of C₁₂-H and C₁₃-H of **1a** at δ 8.21 ppm (in CDCl₃) in the ¹H-NMR spectrum were split into δ 7.84 ppm (d, J=10 Hz) and δ 7.19 ppm (d, J=10 Hz) in the epoxide (**8**), because of disappearance of the symmetry of **1a**.
- 8) F. Yoneda, Y. Sakuma, S. Mizumoto, and R. Ito, *J. Chem. Soc., Perkin Trans. 1*, 1976, 1805.

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