reactivity pattern. Finally, we note that Cl^- abstraction from **1a** in the presence of α-methylstyrene as solvent resulted in the alkylation of the olefin to α-methyl-β-benzylstyrene.[9]

The abstraction of I^- from *trans*-$Pd(PPh_3)_2(I)(CH_3)$ (**2a**)[5] by the addition of 1 equiv of $AgBF_4$ in C_6D_6 at 85 °C resulted in the immediate formation of $PPh_3Me^+BF_4^-$ as the only product[10] (eq 4). The same product was also observed when the cationic compound *trans*-$Pd(PPh_3)_2(CD_3CN)(Me)^+BF_4^-$ (**2b**-CD_3CN), formed through the reaction of **2a** with $AgBF_4$ in CD_3CN, was heated to 50 °C in $CDCl_3$, (eq 5). This reaction appeared to

$$Pd(PPh_3)_2(I)(Me) \xrightarrow[C_6D_6,\ 85\ °C]{AgBF_4} PPh_3Me^+ \quad (4)$$

$$Pd(PPh_3)_2(CD_3CN)(Me)^+ \xrightarrow[CDCl_3,\ 50\ °C]{} PPh_3Me^+ \quad (5)$$

involve the initial dissociation of the CD_3CN ligand, since under identical conditions, no $PPh_3Me^+BF_4^-$ was observed when ca. 10 equiv of CD_3CN was added to the reaction mixture. The addition of 1 equiv of PPh_3 to a $CDCl_3$ solution of **2b**-CD_3CN resulted in the formation of $Pd(PPh_3)_3(Me)^+BF_4^-$ (**2c**). In a subsequent reaction, **2c** was found to decompose at 25 °C in $CDCl_3$ also to $PPh_3Me^+BF_4^-$.

The reactivity of the methyl compounds as encompassed by eq 4 and 5 clearly differed significantly from that of the benzyl compounds (eq 2 and 3). The difference between eq 3 and 5 is presumably a reflection of the relatively greater stability of the $PhCH_2^{\bullet}$ radical. The origin of the difference between eq 2 and 4 is less certain but may be related to the greater stabilization of the $PhCH_2^+$ cation. Like the methyl group, the vinyl group also forms poorly stabilized cations and radicals and the phosphonium cation was also the preferred decomposition product for the vinyl compounds. For example, the cationic compounds *trans*-$Pd(PPh_3)_2(CD_3CN)((E)\text{-}COCR{=}CHR')^+BF_4^-$ (R = Me, R′ = H; R = H, R′ = Me) were found to decompose quantitatively at 25 °C in $CDCl_3$ in a few hours to the corresponding phosphonium salts, presumably by an initial deinsertion of CO (eq 6).

$$Pd(PPh_3)_2(CD_3CN)((E)\text{-}COCR{=}CHR')^+ \xrightarrow[CDCl_3,\ 25\ °C]{-CO} PPh_3\{(E)\text{-}CR{=}CHR')^+ \quad (R = Me, R' = H; R = H, R' = Me) \quad (6)$$

Finally, the radical decomposition pathway was also available for the non-benzylic alkyl compounds if the formation of the phosphonium salt was precluded. For example, CMe_4 was the sole decomposition product when *cis*-$Pd(bpy)(CH_3CN)(CH_2CMe_3)^+BF_4^-$, formed by the reaction of 1 equiv of $AgBF_4$ with *cis*-$Pd(bpy)(Br)(CH_2CMe_3)$[11] in CH_3CN, was heated in $CDCl_3$ at 70 °C (eq 7). The absence of any rearrangement of the neopentyl group appeared to exclude the intermediacy of carbocations in this reaction.

$$Pd(bpy)(CH_3CN)(CH_2CMe_3)^+ \xrightarrow[CDCl_3,\ 70\ °C]{} CMe_4 \quad (>98\%\ d_0) \quad (7)$$

In conclusion, we have demonstrated (a) the surprising diversity of radical and nonradical pathways that exists for the decomposition of monoalkyl complexes of the later transition metals and (b) how the preferred pathway is a function of the alkyl group, the nature of the complex, and the reaction conditions.

Acknowledgment. We thank Dr. Jeffrey S. Brumbaugh for several experiments and helpful discussions. The research was supported by grants from the National Science Foundation (CHE-8312380) and the U.S. Department of Energy, Office of Basic Energy Sciences (DE-FGO2-84ER13295), and by a generous loan of $PdCl_2$ from Johnson Matthey, Inc.

(9) This reaction resembled the Heck procedure for the alkylation of olefins which is believed to involve the intermediacy of Pd(II) alkyl species, see: Heck, R. F. *Organotransition Metal Chemistry: A Mechanistic Approach*; Academic Press: New York, 1974; Chapter 5.

(10) The reductive elimination of the phosphonium cation has been observed previously; see: Kampmeier, J. A.; Harris, S. H.; Rodehorst, R. M. *J. Am. Chem. Soc.* **1981**, *103*, 1478 and references therein.

(11) Diversi, P.; Fasce, D.; Santini, R. *J. Organomet. Chem.* **1984**, *269*, 285.

Registry No. 1a, 22784-59-4; **1c**-CD_3CN, 103712-41-0; **2a**, 18115-58-7; **2b**-CD_3CN, 103712-43-2; **2c**, 103712-45-4; $[Pd(PPh_3)(CH_2Ph)(\mu\text{-}Cl)]_2$, 22784-54-9; $C_6D_5CH_2C_6H_5$, 103730-93-4; *o*-$CD_3C_6D_4CH_2C_6H_5$, 103730-94-5; *p*-$CD_3C_6D_4CH_2C_6H_5$, 103730-95-6; $C_6H_5CH_2CH_2C_6H_5$, 103-29-7; $PPh_3Me^+BF^-$, 2793-21-7; $Pd(PPh_3)_2(CD_3CN)(COC(CH_3){=}CH_2)^+BF_4^-$, 103712-47-6; $Pd(PPh_3)_2(CD_3CN)((E)\text{-}COCH{=}CH(CH_3))^+BF_4^-$, 103712-49-8; $PPh_3(C(CH_3){=}CH_2)^+BF_4^-$, 103730-96-7; $PPh_3((E)\text{-}CH{=}CH(CH_3))^+BF_4^-$, 103730-98-9; CMe_4, 463-82-1; *cis*-$Pd(bpy)(CH_3CN)(CH_2CMe_3)^+BF_4^-$, 103712-51-2; *cis*-$Pd(bpy)(Br)(CH_2CMe_3)$, 92392-00-2; $Pd(PhCN)_2Cl_2$, 14220-64-5; $PhCH_2Cl$, 100-44-7; α-methyl-β-benzylstyrene, 17342-56-2.

Supplementary Material Available: NMR spectral data for Pd(II) compounds and organic products (2 pages). Ordering information is given on any current masthead page.

Photochemical Oxygen Atom Transfer Reaction by Heterocycle *N*-Oxides Involving a Single-Electron-Transfer Process: Oxidative Demethylation of *N*,*N*-Dimethylaniline

Magoichi Sako, Kaoru Shimada, Kosaku Hirota, and Yoshifumi Maki*

Gifu Pharmaceutical University
6-1, Mitahora-higashi 5 Chome, Gifu 502, Japan

Received September 18, 1985

Photochemical oxygen atom transfer reaction by heterocycle *N*-oxides[1] can be considered to be one of the mechanistic model systems of various biological oxidations catalyzed by hepatic monooxygenases, e.g., cytochrome P-450. After extensive investigations, it has been proposed that the reaction is induced by the active oxygen species such as oxene or oxazilidine intermediates arising from the excited *N*-oxides.[2]

In this paper we wish to present a first example of a photochemical oxygen atom transfer reaction by the *N*-oxides proceeding via a single-electron-transfer process which is suggestive of the presence of an alternative process not involving these active oxygen species in the photochemical oxidation by the heterocycle N-oxides.

Irradiation[3] of a mixture of pyrimido[5,4-*g*]pteridine *N*-oxide **1**[4] (5 mM) and *N*,*N*-dimethylaniline (DMA) (50 mM) in dry acetonitrile with UV–visible light at ambient temperature under argon atmosphere afforded the deoxygenated pyrimido[5,4-*g*]-pteridine and *N*-monomethylaniline (MMA) in high yields. No

(1) Streith, J.; Danner, B.; Sigwalt, C. *J. Chem. Soc. D* **1967**, 979. Alkaitis, A.; Calvin, M. *Ibid.* **1968**, 292. Igeta, H.; Tsuchiya, T.; Yamada, M.; Arai, H. *Chem. Pharm. Bull.* **1968**, *16*, 767. Jerina, D. M.; Boyd, D. R.; Daly, J. W. *Tetrahedron Lett.* **1970**, 457. Tsuchiya, T.; Arai, H. Igeta, H. *Ibid.* **1969**, 2747; **1970**, 2213. Nakagawa, M.; Kaneko, T.; Yamaguchi, H. *J. Chem. Soc., Chem. Commun.* **1972**, 603. Nakagawa, M.; Kaneko, T.; Yamaguchi, H.; Kawashima, T.; Hino, T. *Tetrahedron* **1974**, *30*, 2591. Serra-Errante, G.; Sammes, P. G. *J. Chem. Soc., Chem. Commun.* **1975**, 573. Rastetter, W. H.; Gadek, T. R.; Tane, J. P.; Frost, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 2228. Akhtar, M. N.; Boyd, D. R.; Neil, J. D.; Jerina, D. M. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1693. Tokumura, K.; Goto, H. Kashiwabara, H. Kaneko, C.; Itoh, M. *J. Am. Chem. Soc.* **1980**, *102*, 5643. Ito, Y.; Matsuura, T. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1871. Rowely, A. G.; Steedmann, J. R. F. *Chem. Ind. (London)* **1981**, 365. Ogawa, Y.; Iwasaki, S.; Okuda, S. *Tetrahedron Lett.* **1981**, *22*, 2277, 3637.

(2) For recent reviews on the mechanism for photochemistry of the heterocycle *N*-oxides, see: Spence, G. G.; Taylor, E. C.; Buchardt, O. *Chem. Rev.* **1970**, *70*, 231. Albini, A.; Alpegiani, M. *Ibid.* **1984**, *84*, 43.

(3) A 400-W high-pressure mercury arc lamp (Riko Kagaku Sangyo) through Pyrex filter.

(4) Recently, we have demonstrated that the *N*-oxide **1** is an efficient oxygen atom transfer agent; e.g., the *N*-oxide **1** oxidizes benzene, toluene, and anisole under UV irradiation to give the corresponding phenols in high yields: Sako, M.; Shimada, K.; Hirota, K.; Maki, Y. *Tetrahedron Lett.* **1985**, *26*, 6493.

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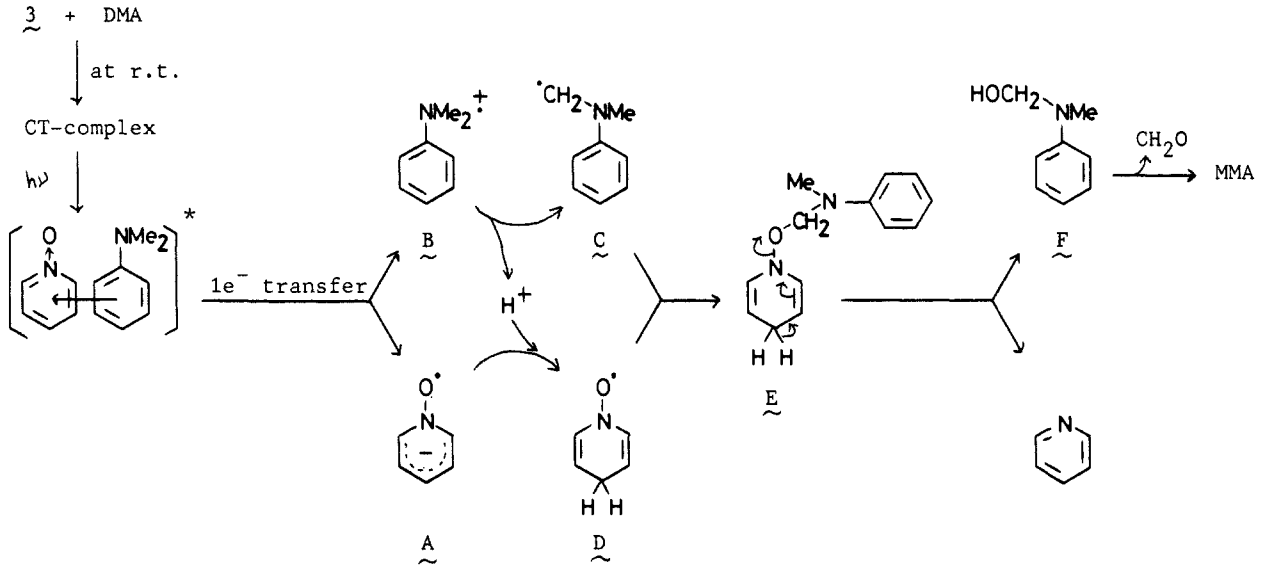
Table I. Photochemical Reaction of Heterocycle *N*-Oxides **1–6** with DMA and Interaction between the *N*-Oxides **1–6** and DMA

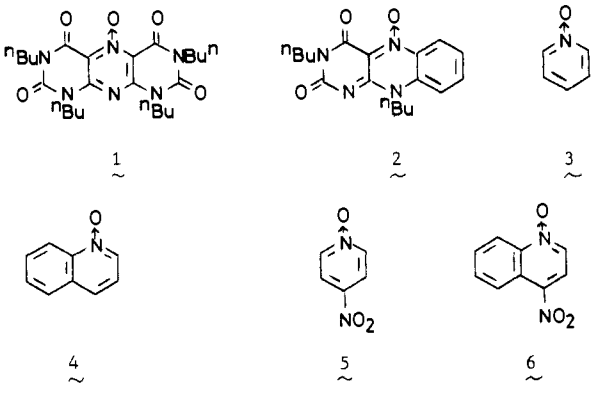
heterocycle *N*-oxide	photoreaction of the *N*-oxide with DMA[a] deoxygenated heterocycle,[b] %	MMA,[c] %	recovered *N*-oxide,[b] %	consumption rate of the *N*-oxide, $10^5k'$, s^{-1}[g] in the absence of DMA	in the presence of DMA	absorptn of CT complex of *N*-oxide with DMA, nm (ϵ)[h] [λ_{max} of *N*-oxide][i]
1	75[d]	72	9	0.6	36.2	412 (118) [370]
2	50[e]	47	43	24.6	11.9	518 (82) [475]
3	9	9				332 (516) [276]
4	trace	11	90	4.4	1.5	[350]
5	4[f]	70[f]	39	3.1	14.0	396 (42)[j] [345]
6	3[f]	23[f]	62	8.4	6.7	433 (72)[k] [384]

[a] A mixture of heterocycle *N*-oxide **1–6** (5 mM) and DMA (50 mM) in MeCN was irradiated by using 400-W high-pressure mercury arc lamp through Pyrex filter under argon atmosphere for 2 h. [b] Isolated yield. [c] By GC analysis. [d] Mp 113–116 °C (from EtOH–H_2O). [e] Mp 188–191 °C (from AcOEt). [f] Kaneko, C.; Yamamoto, A.; Gomi, M. *Heterocycles* **1979**, *12*, 227. The deoxygenated products, 4-nitropyridine and 4-nitroquinoline, further oxidized DMA to give MMA, though the reaction was not efficient (25–37% yield, under the conditions analogous to the case of the *N*-oxides). [g] A solution of the *N*-oxide **1–6** (5 mM) in MeCN was irradiated by using Riko Rotary Photochemical Reactor Model RH 400-10W (400-W high-pressure mercury arc lamp) through Pyrex filter under argon atmosphere in the absence or presence of DMA (50 mM). [h] Heterocycle *N*-oxide **1–6** (5 mM), DMA (250 mM), in MeCN, at 21 °C. [i] In MeCN. [j] 413 nm in $ClCH_2CH_2Cl$ at 25 °C; cf. ref 7. [k] 438 nm (243) in $ClCH_2CH_2Cl$, at 25 °C; cf. ref 7.

Scheme I



formation of other products, except formaldehyde, in this reaction was shown by TLC and GC analyses of the reaction mixture.[5] The reaction did not proceed in the dark (reflux for 8 h), clearly indicating that irradiation is requisite for the completion of the reaction. Thus, the demethylation of DMA by **1** takes place efficiently under irradiation with UV–visible light.



The consumption rate of **1** in dry acetonitrile under irradiation was significantly affected by the presence of DMA as shown in Table I. The stability of **1** toward UV–visible light and the remarkable effect of DMA on the consumption rate of **1** suggest that there would be an interaction between **1** and DMA in the above reaction. Ground-state charge-transfer interaction between **1** and DMA was observed as evidenced by UV–visible absorption spectrum (see Figure 1). A strong wavelength dependence was observed in this photoreaction and excitation of the **1**/DMA complex (412 nm) resulted in a maximum yield of the products, pyrimido[5,4-*g*]pteridine and MMA. Analogous demethylation of DMA was also observed by employment of other heterocycle *N*-oxides such as 3,10-di-*n*-butylisoalloxazine *N*-oxide (**2**),[6] pyridine *N*-oxide (**3**), quinoline *N*-oxide (**4**), 4-nitropyridine *N*-oxide (**5**), and 4-nitroquinoline *N*-oxide (**6**) in place of **1** as summarized in Table I, though the stability of the *N*-oxides toward the UV–visible light and the ease of the reaction were significantly dependent on the nature of the *N*-oxides employed.

Taking the above facts and the reported substantiation on the

(5) The reaction did not produce a detectable amount of DMA *N*-oxide and *N*-formyl-*N*-methylaniline which are stable under the reaction conditions. It has been already demonstrated that the formation of *N*-formyl-*N*-methylaniline is observed in the photochemical reaction of aromatic nitro compounds with DMA. cf.: Takami, M.; Matsuura, T.; Saito, I. *Tetrahedron Lett.* **1974**, 661.

(6) The *N*-oxide **2** was prepared with ease from 3-butyl-6-*N*-butyl-anilinopyrimidine-2,4(1*H*,3*H*)-dione according to the Yoneda's procedure: mp 185–188 °C (from benzene–diethyl ether); IR (KBr) 1700, 1660 (C=O) cm^{-1}; UV(MeCN) 475 (5×10^3), 451 (6×10^3), 339 (8×10^3), 269 (2.7×10^4), 212 (9.2×10^3); ^1H NMR ($CDCl_3$) δ 0.75–1.20 (6 H, m), 1.20–2.25 (8 H, m), 4.04 (2 H, br, t), 4.69 (2 H, br t), 7.25–8.75 (4 H, m); MS, *m/e* 342 (M^+), 326, 228, 215. Cf.: Yoneda, F.; Sakuma, Y.; Ichiba, M.; Shinomura, K. *J. Am. Chem. Soc.* **1976**, *98*, 830.

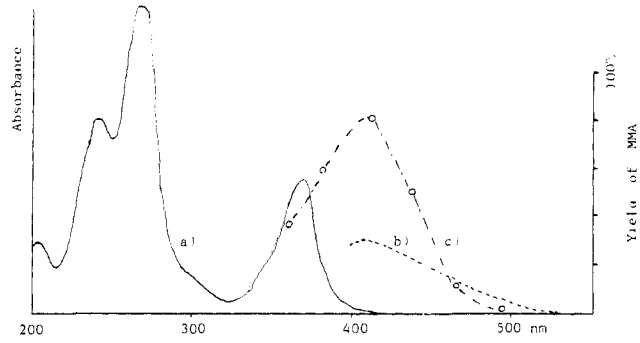


Figure 1. (a) UV-visible absorption spectrum of pyrimido[5,4-*g*]pteridine *N*-oxide **1** (5×10^{-5} M) in MeCN. (b) Difference spectrum of the mixture of **1** (5 mM) and DMA (250 mM) vs. **1** (5 mM) in MeCN. (c) Wavelength dependence (presented by the yield of MMA) in the photochemical demethylation of DMA by **1**. A solution of **1** (5 mM) and DMA (50 mM) in MeCN was irradiated by using a grating monochromator (JASCO Model CRM-FA) with 2-kW Xe lamp and 4-nm band width under argon atmosphere for 2 h.

CT complex formation of the *N*-oxides **5** and **6** with DMA[7] into consideration, a plausible mechanism for the present demethylation of DMA by the *N*-oxides **1**–**6** is depicted in Scheme I by using for an example the case of **3**.

The reaction could be initiated by the formation of the *N*-oxide/DMA charge-transfer complex in a ground state followed by a single-electron transfer from DMA to the *N*-oxides in the excited complex to give the *N*-oxide radical anion A and anilinium radical cation B. Subsequent steps of proton transfer from B to A generating *N*-methyl radical C and nitroxyl radical D, coupling of the resulting radical C with D leading to a transient adduct E, and heterocyclic fragmentation of N–O bond in E give the deoxygenated heterocycles and carbinolamine F.[8] Elimination of formaldehyde from F would produce the final demethylated product (MMA). In agreement with the proposed electron-transfer mechanism, the addition of *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD)[9] or tetracyanoethylene into the reaction media of **1** with DMA inhibited the formation of MMA even at very low concentration (0.1 equiv to **1**). The present result formally parallels the mechanism proposed for the cytochrome P-450 catalyzed N-dealkylation which involves an initial single-electron-transfer process.[10]

Acknowledgment. We express our grateful acknowledgment to Dr. M. Kuzuya of our university for invaluable discussions.

Registry No. 1, 33070-58-5; **1** (deoxygenated), 103620-51-5; **2**, 103620-50-4; **3**, 694-59-7; **3** (deoxygenated), 110-86-1; **4**, 1613-37-2; **5**, 1124-33-0; **5** (deoxygenated), 1122-61-8; **6**, 56-57-5; **6** (deoxygenated), 3741-15-9; DMA, 121-69-7; MMA, 100-61-8; CH_2O, 50-00-0.

(7) Okano, T.; Uekama, K.; Isawa, Y.; Tsukuda, K. *Yakugaku Zasshi* **1967**, *87*, 1309. Okano, T.; Miura, T.; Yoshida, M.; Uekama, K. *Ibid.* **1969**, *89*, 1379. Kubota, T.; Akazawa, H.; Yamakawa, M. *Chem. Lett.* **1972**, 1147.

(8) Another possible mechanism for the formation of F can be considered, involving the addition of water arising from D to the iminium ion species generating from C after further redox reaction between C and D. This stepwise mechanism, however, is less favorable because the photoreaction of **1** with DMA in acetonitrile containing methanol in various concentrations did not afford *N*-(methoxymethyl)-*N*-methylaniline which could be formed as a result of capture of the generated iminium ion species by methanol. Cf.: Miyata, N.; Kiuchi, H.; Hirobe, M. *Chem. Pharm. Bull.* **1981**, *29*, 1489.

(9) When a solution of **1** and TMPD in dry acetonitrile was irradiated, the absorption (568 and 612 nm) of the well-known TMPD radical cation was observed. The present result suggests that **1** possesses a one-electron-accepting ability in the photoreaction conditions. Cf.: Michaelis, L.; Schubert, M. P.; Granick, S. *J. Am. Chem. Soc.* **1939**, *61*, 1981. Franzen, V. *Chem. Ber.* **1955**, *88*, 1697.

(10) Hanzlik, R. P.; Tullman, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 2048. Macdonald, T. L.; Zirvi, K.; Burka, L. T.; Peyman, P.; Guengerich, F. P. *Ibid.* **1982**, *104*, 2050. Guengerich, F. P.; Macdonald, T. L. *Acc. Chem. Res.* **1984**, *17*, 9. Miwa, G. T.; Walsh, J. S.; Kedderis, G. L.; Hollenberg, P. F. *J. Biol. Chem.* **1983**, *258*, 14445. Lindsay Smith, J. R.; Mortimer, D. N. *J. Chem. Soc., Chem. Commun.* **1985**, 64. Burka, L. T.; Guengerich, F. P.; Willard, R. J. Macdonald, T. L. *J. Am. Chem. Soc.* **1985**, *107*, 2549.

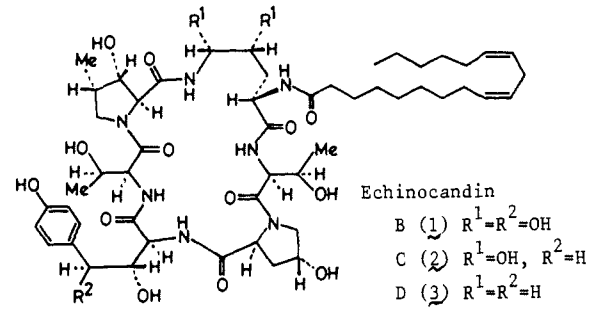
Total Synthesis of Echinocandins. 1. Stereocontrolled Syntheses of the Constituent Amino Acids

Natsuko Kurokawa and Yasufumi Ohfune*

Suntory Institute for Bioorganic Research
Shimamoto-cho, Mishima-gun, Osaka 618, Japan

Received April 14, 1986

Echinocandins isolated from a strain of *Aspergillus ruglosus* and *Aspergillus nidulans* are novel oligopeptide antibiotics characterized by their high antifungal and antiyeast activities.[1-3] Recently, their potent effectiveness against candidosis has been examined.[4] The structure of echinocandin B determined by chemical degradation studies in combination with the X-ray crystallographic analysis of its derivative was found to be an unique 21-membered cyclic lipopeptide as shown in **1**.[2,5] The structures of echinocandin C (**2**) and D (**3**) were elucidated by converting them into a common intermediate derived from **1**.[6]



On the basis of our previous results related to the stereoselective syntheses of biologically active amino acids starting from vinylglycine equivalent **5a** and allylglycine derivative **6a** as the chiral building blocks,[7] we focused our attention on the synthesis of peptides constructed from unusual amino acids, where synthetic methods are extremely limited. Since **1** is chemically unstable in the presence of a benzylic hydroxyl group,[8] echinocandin C and D were chosen for the present study. Described, herein, are the stereocontrolled syntheses of the constituent amino acids. The following paper will describe the total synthesis of echinocandin D (**3**).[9] All constituent amino acids in **2** and **3** are composed of β- and/or γ-substituted α-amino acids. Initially, the strategies to synthesize the amino acids were from the acyclic precursors **4a**, **5b**, and **6a**.

Synthesis of (2*S*,3*S*,4*S*)-3-Hydroxy-4-methylproline (4). Disconnection of the pyrrolidine ring at the C5–N bond provides the acyclic intermediate **4c**, in which the consecutive 3*S*,4*S* chiral centers corresponded to those of a known epoxy alcohol **4a**.[10]

(1) Benz, F.; Knüsel, F.; Nüesch, J.; Treichler, H.; Voser, W.; Nyfeler, R.; Keller-Schierlein, W. *Helv. Chim. Acta* **1974**, *57*, 2459.

(2) Keller-Juslén, C.; Kuhn, M.; Loosli, H.-R.; Petcher, T. J.; Weber, H. P.; von Wartburg, A. *Tetrahedron Lett.* **1976**, 4147.

(3) Related compounds have been isolated: (a) Mizuno, K.; Yagi, A., Satoi, S.; Takada, M.; Hayashi, M.; Asano, K.; Matsuda, T. *J. Antibiot.* **1977**, *30*, 297. (b) Satoi, S.; Yagi, A.; Asano, K.; Mizuno, K.; Watanabe, T. *J. Antibiot.* **1977**, *30*, 303. (c) Abbott, B. J.; Fukuda, D. S. US Patent **1981**, 4 293 482 and 4 293 490. (d) Kotani, M.; Satoi, S.; Takada, M. Japanese Patent **1979**, 54-160301.

(4) (a) Mizoguchi, J.; Saito, T.; Mizuno, K.; Hayano, K. *J. Antibiot.* **1977**, *30*, 308. (b) Bagnley, B. C.; Rommele, G.; Gruner, J.; Wehrli, W. *Eur. J. Biochem.* **1979**, *97*, 345.

(5) Koyama, G. *Helv. Chim. Acta* **1974**, *57*, 2477.

(6) Traber, R.; Keller-Juslén, C.; Loosli, H.-R.; Kuhn, M.; von Wartburg, A. *Helv. Chim. Acta* **1979**, *62*, 1252.

(7) (a) Ohfune, Y.; Kurokawa, N. *Tetrahedron Lett.* **1984**, 1071. (b) Ohfune, Y.; Kurokawa, N. *Tetrahedron Lett.* **1984**, 1587. (c) Ohfune, Y.; Nishio, H. *Tetrahedron Lett.* **1984**, 4133. (d) Kurokawa, N.; Ohfune, Y. *Tetrahedron Lett.* **1985**, 83. (e) Ohfune, Y.; Kurokawa, N. *Tetrahedron Lett.* **1985**, 5307.

(8) Keller-Schierlein, W.; Joos, B. *Helv. Chim. Acta* **1980**, *63*, 250.

(9) Kurokawa, N.; Ohfune, Y. *J. Am. Chem. Soc.* **1986**, *108*, following paper.

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