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PHOTOOXYGENATION OF PTERIDIN-2,4,7-TRIONES

Takehiko Nishio*, Tadashi Nishiyama, and Yoshimori Omote

Department of Chemistry, University of Tsukuba, Tsukuba-shi, Ibaraki 305, Japan

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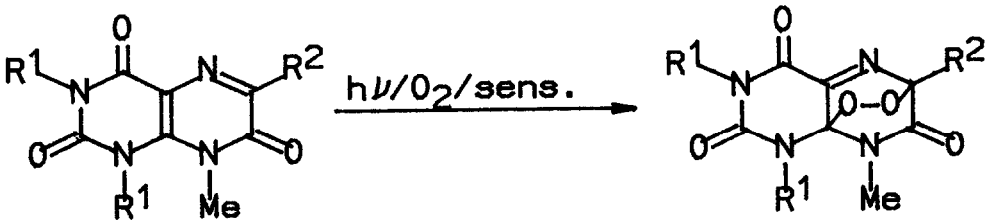
Summary: The pteridin-2,4,7-trione 6,8'-endoperoxides are synthesized and their thermal reactions are examined. The pteridin-2,4,7-triones (**1**) reacted smoothly with singlet oxygen to yield the pteridin-2,4,7-trione 6,8'-endoperoxides (**2-5**). On warming the endoperoxide (**2a**) reverted to the starting pteridin-2,4,7-trione (**1a**) with liberation of singlet oxygen, which was confirmed by trapping experiment using typical singlet oxygen acceptors (**7-12**).

Singlet oxygen is known to react with different types of heterocyclic compounds, giving rise to a variety of products depending on the nature of substrates, primary photooxygenation products such as the peroxide and hydroperoxide, and reaction conditions. However, additions of singlet oxygen to heterocycles containing nitrogen atoms are largely limited to five-membered ring systems such as pyrrole, indole, imidazole, and purine derivatives.[1,2] The formation of endoperoxides of six-membered nitrogen heterocycles such as pyrazines,[3] pyrimidines,[3] 1,2-dihydropyridines,[4], pyridinium-4-olates,[5] and 2-pyridones[6] has been described. Recently, we reported the dye-sensitized photooxygenation of N-substituted pyrazin-2-ones, which gave the stable pyrazin-2-one 3,6-endoperoxides,[7] and additions of singlet oxygen to alkoxypyrazines.[8] Furthermore, dye-sensitized photooxygenation of uracil derivatives in liquid ammonia at low temperature has been reported to give an unstable peroxy intermediate, which on warming fragments to give a complex mixture.[9] We report herein that the pteridin-2,4,7-triones (**1**), which possess both uracil and pyrazinone skeletons, can absorb singlet oxygen smoothly to yield the stable endoperoxides (**2-5**) and on warming the endoperoxide (**2a**) reverts to the starting pteridin-2,4,7-trione (**1a**) with the liberation of singlet oxygen.[10]

RESULTS AND DISCUSSION

Dye-sensitized Photooxygenation of the Pteridin-2,4,7-triones (1).

Irradiation of an oxygenated solution of 6-phenyl-1,3,8-trimethylpteridin-2,4,7-trione (**1a**) in dichloromethane in the presence of rose bengal as a sensitizer with visible light at room temperature for 2 h gave 6-phenyl-1,3,8-trimethylpteridin-2,4,7-trione 6,8'-endoperoxide (**2a**) in 79% isolated yield. The structure of **2a** was confirmed on the basis of spectral properties and elemental analysis. The pteridin-2,4,7-trione 6,8'-endoperoxide (**2a**) was also obtained in 71% yield when the polymer-based rose bengal,[11] which is known to be efficient as a sensitizer in non-polar solvents such as dichloromethane, was used for the photooxygenation of 1a. The endoperoxide (**2a**) thus obtained is indefinitely stable at room temperature in the solid state. Meanwhile, irradiation of an oxygenated solution of 1a in methanol in the presence of rose bengal or methylene blue as a sensitizer under the same conditions as described above gave the 5'-methoxypteridin-2,4,7-trione 6,8'-endoperoxide (**4a**), which was the 1:1-adduct of **2a** and methanol.



1

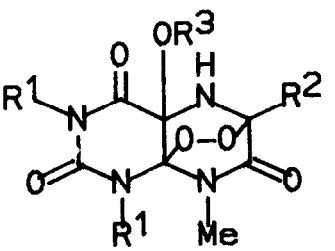
a: R^1=Me R^2=Ph

b: R^1=Me R^2=Me

c: R^1=Ph R^2=Me

d: R^1=Ph R^2=Ph

2



3 R^3=H

4 R^3=Me

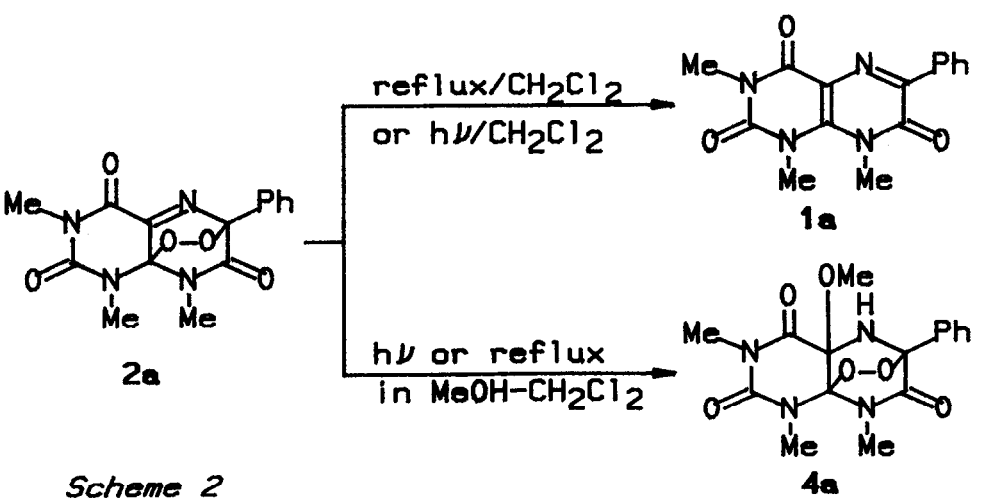
5 R^3=Et

Scheme 1

Table 1. Yield of endoperoxides (2-5)

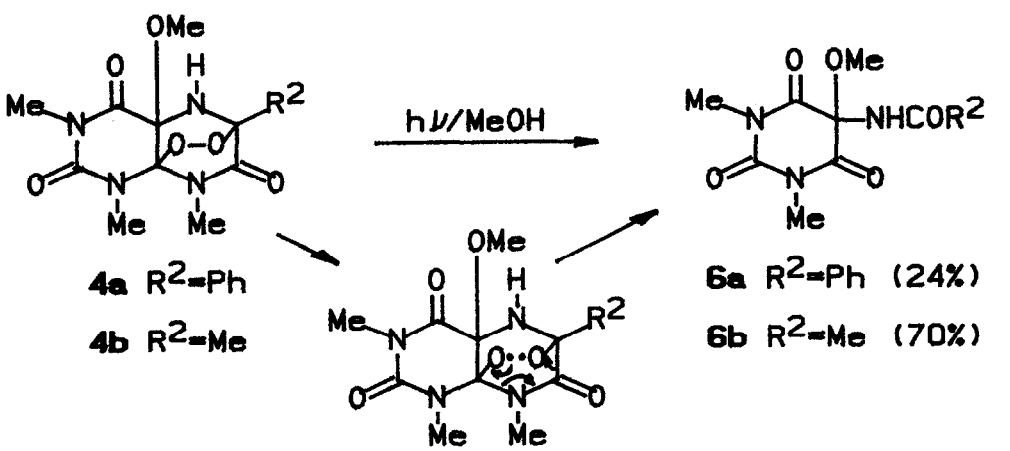
	R^1	R^2	Sens.	Solvent	Irr. time (h)	Yield (%)[a] 2	3	4	5
1a	Me	Ph	RB[b]	CH_2Cl_2	2	79			
1a			p-RB[c]	CH_2Cl_2	2	71			
1a			RB	MeOH	2			83	
1a			MB[d]	MeOH	2			93	
1a			MB	CH_2Cl_2-EtOH	2	63			
1a			MB	CH_2Cl_2-t-BuOH	2	72			
1b	Me	Me	RB	CH_2Cl_2	2		21		
1b			MB	CH_2Cl_2	2		75		
1b			RB	MeOH	2			83	
1b			MB	MeOH	2			73	
1b			RB	CH_2Cl_2-t-BuOH	2		8		
1c	Ph	Me	RB	CH_2Cl_2	10	0[e]			
1c			p-RB	CH_2Cl_2	4	20			
1c			MB	CH_2Cl_2	1	0[e]			
1c			MB	MeOH	1			85	
1c			MB	CH_2Cl_2-EtOH	1				39
1d	Ph	Ph	RB	CH_2Cl_2	10	0[e]			
1d			p-RB	CH_2Cl_2	4	58			
1d			MB	CH_2Cl_2	10	21			

[a]Isolated yield. [b]Rose bengal. [c]Polymer-based rose bengal. [d]Methylene blue. [e]Intractable mixture.



Scheme 2

The yield of **4a** was drastically reduced to 38% by the addition of singlet oxygen quencher, 1,4-diazabicyclo[2.2.2]octane (DABCO). This dihydro-endoperoxide (**4a**) was also produced in almost quantitative yield when the endoperoxide (**2a**) was refluxed[12] or irradiated with a high-pressure mercury lamp in methanol. Upon irradiation the dihydro-endoperoxides (**4a,b**) yielded barbituric acid derivatives (**6a,b**), while **4a** was heated to reflux in methanol to give an intractable mixture. The formation of **6** can be rationalized in terms of the biradical intermediate (**B**) by O-O bond homolysis of **4** and its further fragmentation as shown in Scheme 3. However, incorporation of ethanol or t-butanol was not observed when the dye-sensitized photooxygenation was carried out in dichloromethane-ethanol or dichloromethane-t-butanol,[13] probably due to the steric reason. Irradiation of an oxygenated solution of 1,3,6,8-tetramethylpteridin-2,4,7-trione (**1b**) in dichloromethane in the presence of a sensitizer (rose bengal or methylene blue) under the same conditions gave the 5'-hydroxy-pteridin-2,4,7-trione 6,8'-endoperoxide (**3b**), but the endoperoxide (**2b**) was not isolated. The formation of **3b** can be explained in terms of the addition of water to the endoperoxide (**2b**), initially formed by the reaction of the pteridin-2,4,7-trione (**1b**) with singlet oxygen, during the work-up for purification.[14] The formation of the endoperoxide (**2b**) was confirmed by NMR spectra (see experimental section). Methanol-adduct (**4b**) of the endoperoxide (**2b**) was also produced in high yields when dye-sensitized photooxygenation of **1b** was carried out in methanol.

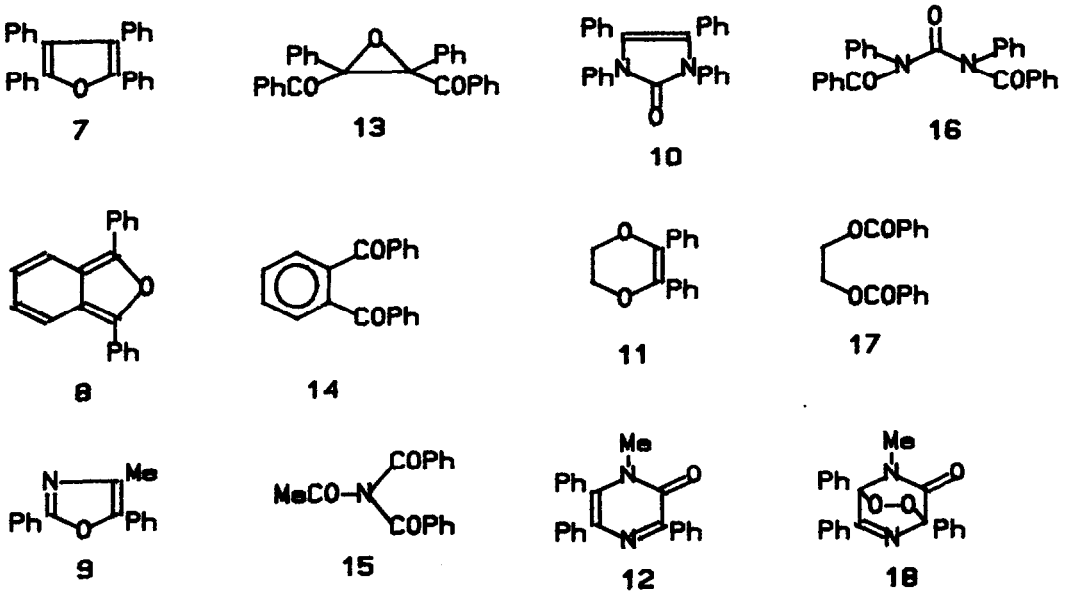


Scheme 3

Similarly, the pteridin-2,4,7-triones (**1c,d**) reacted with singlet oxygen to give the corresponding endoperoxides (**2c,d**), but in low yields. In methanol, the pteridin-2,4,7-trione (**1c**) readily underwent the dye-sensitized photooxygenation to yield the methanol-adduct (**4c**). In the case of **1c**, 1:1-adduct (**5c**) of ethanol with endoperoxide (**2c**) was isolated in 39% yield.

Thermal Reactions of 6-Phenyl-1,3,8-trimethylpteridin-2,4,7-trione 6,8'-Endoperoxide (2a).

The pteridin-2,4,7-trione 6,8'endoperoxide (**2a**) is indefinitely stable at room temperature in the solid state as mentioned above. However, upon heating to reflux in dichloromethane **2a** reverted to the starting pteridin-2,4,7-trione (**1a**) in almost quantitative yield with a concomitant formation of singlet oxygen. The formation of singlet oxygen in the thermal reaction was confirmed by trapping with a variety of known singlet oxygen acceptors.[7,15-18,19a,c] (Table 2) A solution of the endoperoxide (**2a**) and a singlet oxygen acceptor, tetraphenylfuran (**7**), (1:1 mole ratio) in dichloromethane was heated to reflux for 4 h under an argon atmosphere to yield cis-dibenzoylstilbene oxide (**13**)[15] and the pteridin-2,4,7-trione (**1a**) in 82% and quantitative yields, respectively. Similar results were obtained when the thermal reaction was carried out in various mole ratios (2:1-10:1) of 2a and acceptor (**7**).

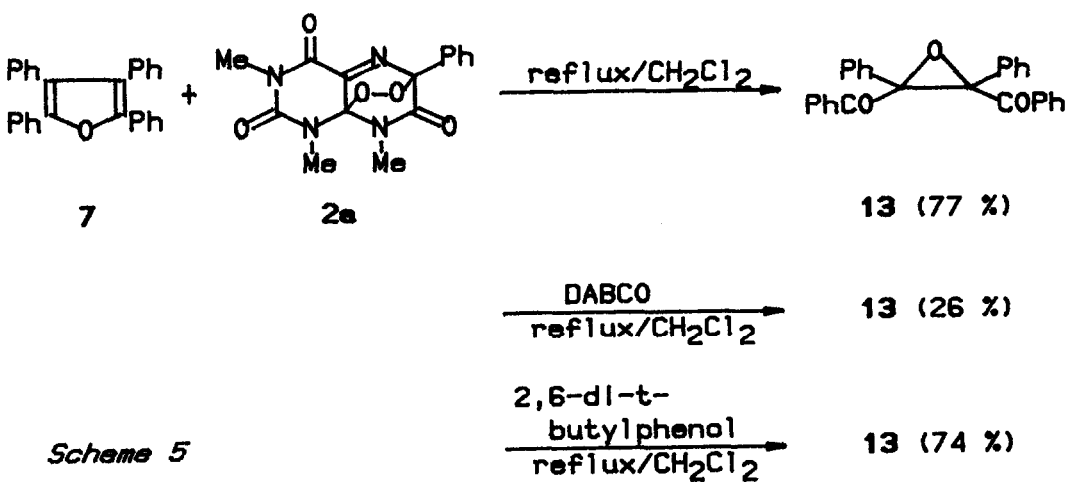


Scheme 4

Table 2. Thermal Decomposition of 6-Phenyl-1,3,8-trimethylpteridin-2,4,7-trione 6,8'-Endoperoxide (**2a**) in the Presence of Singlet Oxygen Acceptors (7-12)

Acceptor	Mole ratio of **2a** to acceptor	Product (yield, %)[a]	Photosensitized oxygenation[b] (yield, %)[c]
7	1:1	**13** (82)	**13** (57)
	2:1	(84)	
	5:1	(73)	
	10:1	(77)	
8	1:1	**14** (88)	**14** (84)
	5:1	(85)	
	10:1	(81)	
9	1:1	**15** (58)	**15** (90)
	10:1	(84)	
10	1:1	**16** (70)	**16** (35)
	10:1	(32)	
11	1:1	**17** (0)	**17** (72)
	10:1	(77)	
12	1:1	**18** (82)	**18** (96)
	10:1	(86)	

[a]The yields were based on acceptors used. In every cases, the pteridin-2,4,7-trione (**1a**) was produced in almost quantitative yield. [b]Photosensitized oxygenation was carried out in dichloromethane using methylene blue as a sensitizer under an oxygen atmosphere. [c]Isolated yield.



Scheme 5

When a singlet oxygen quencher, DABCO, was added to the reaction system, the yield of the oxidized product (**13**) was drastically reduced. In contrast, the addition of a free radical inhibitor, 2,6-di-tert-butylphenol, did not affect the yield of **13**. (Scheme 5) These results undoubtedly indicate that the reactive species generated by thermal reaction of the endoperoxide (**2a**) is singlet oxygen. Similarly, singlet oxygen thus generated from the endoperoxide (**2a**) was trapped with a variety of typical singlet oxygen acceptors such as 1,3-diphenyl-isobenzofuran (**8**),[16,19a] 2,5-diphenyl-4-methyloxazole (**9**),[17,19a] tetraphenylimidazolinone (**10**),[19c] 2,3-diphenyl-p-dioxene (**11**),[18] and 1-methyl-3,5,6-triphenylpyrazin-2-one (**12**)[7] to give the corresponding oxidized products (**14-18**), along with the parent pteridin-2,4,7-trione (**1a**). The products (**13-18**) isolated were identical with those formed in parallel dye-sensitized photooxygenation of acceptors (**7-12**) and were characterized by direct comparison of their IR and NMR spectra with those of authentic materials.[15-18,19a,c] In every cases, the yields of the oxidized products (**13-18**) were very close to those observed in dye-sensitized photooxygenation of acceptors (**7-12**). (Table 2) Thus, the present method provides a useful chemical mean of producing singlet oxygenation,[19] since the pteridin-2,4,7-trione 6,8'-endoperoxide (**2a**) is stable in solid form and can be stored indefinitely at room temperature.

EXPERIMENTAL SECTION

Melting points are uncorrected. The IR spectra were obtained on a Hitachi 260-30 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL FX-100 (100 MHz) spectrometer. Mass spectra were obtained on a JEOL JMS-DX 300 spectrometer. Silica gel (Merck Kieselgel 60 or Wakogel C-300 for flash chromatography) was used for column chromatography.

Pteridine-2,4,7-triones (**1**) were prepared according to the earlier reported procedure.[20]

General procedure for the Dye-sensitized Photooxygenation of the pteridin-2,4,7-triones (1) in Dichloromethane: An oxygenated solution of the pteridine-2,4,7-trione (**1**) (200 mg) in dry dichloromethane (70 ml) in the presence of sensitizers such as methylene blue, rose bengal, and polymer-based rose bengal (ca 2 mg) was irradiated in a Pyrex vessel with a halogen lamp for 1-10 h at room temperature. After removal of the solvent, the residue was chromatographed on a silica gel column with benzene-ethyl acetate (1:4-ethyl acetate only) to afford the corresponding endoperoxides (**2,3**).

6-Phenyl-1,3,8-trimethylpteridin-2,4,7-trione 6,8'-Endoperoxide (2a); m.p.

278-279 °C; IR(KBr) 1735, 1715, 1680 cm^{-1}; $\delta_H(CDCl_3)$ 3.18 (3H, s), 3.28 (3H, s), 3.37 (3H, s), 7.56-7.73 (3H, m), 7.88-7.99 (2H, m); $\delta_C(CDCl_3)$ 28.5(q), 29.2(q), 31.9(q), 91.6(s), 93.3(s), 128.6(d), 128.9(d), 129.1(s), 130.9(d), 150.1(s), 154.6(s), 161.4(s), 166.7(s). (Anal. Calcd. for $C_{15}H_{14}N_4O_5$: C, 54.54; H, 4.27; N, 16.96. Found: C, 54.66; H, 4.27; N, 16.96%).

1,3,6,8-Tetramethylpteridin-2,4,7-trione 6,8'-Endoperoxide (2b); IR(KBr) 1715, 1685 cm^{-1}; $\delta_H(CDCl_3)$ 1.93 (3H, s), 2.99 (3H, s), 3.20 (3H, s), 3.38 (3H, s); $\delta_C(CDCl_3)$ 16.5(q), 28.2(q), 28.8(q), 31.6(q), 90.8(s), 93.2(s), 149.7(s), 154.1(s), 160.3(s), 167.3(s).

6,8-Dimethyl-1,3-diphenylpteridin-2,4,7-trione 6,8'-Endoperoxide (2c); IR($CHCl_3$) 1740, 1680 cm^{-1}; $\delta_H(CDCl_3)$ 2.57 (3H, s), 3.08 (3H, s), 7.04-7.55 (10H, m); m/z(CI) 393 ($M^+ + 1$).

8-Methyl-1,3,6-triphenylpteridin-2,4,7-trione 6,8'-Endoperoxide (2d); IR($CHCl_3$) 1730, 1695 cm^{-1}; $\delta_H(CD_3OD)$ 3.01 (3H, s), 7.12-7.77 (15H, m); $\delta_C(CD_3OD)$ 26.2(q), 80.0(s), 97.0(s), 127.3(d), 127.6(d), 128.3(d), 129.0(s), 129.7(s), 130.0(d), 130.2(d), 130.4(s), 131.0(d), 134.4(d), 151.9(s), 155.3(s), 165.6(s), 168.7(s).

The endoperoxides (**2b-d**) could not be obtained in analytical pure state since these products gradually decomposed during purification by a silica gel column chromatography.

1,3,6,8-Tetramethyl-5'-hydroxypteridin-2,4,7-trione 6,8'-Endoperoxide (3b); m.p. 156-157 °C(dec.); IR(KBr) 3315, 1715, 1695, 1670 cm^{-1}; δ_H(DMSO-d_6) 1.56 (3H, s), 3.17 (3H, s), 3.19 (3H, s), 3.26 (3H, s), 5.76 (1H, br s), 7.61 (1H, br s); δ_C(DMSO-d_6) 15.4(q), 28.3(q), 32.1(q), 33.1(q), 77.7(s), 88.0(s), 97.6(s), 152.2(s), 166.6(s), 167.7(s). (Anal. Calcd. for $C_{10}H_{14}N_4O_6$: C, 41.96; H, 4.93; N, 19.57. Found: C, 41.76; H, 4.98; N, 19.47%).

General Procedure for the Dye-sensitized Photooxygenation of the Pteridin-2,4,7-triones (1) in Alcohol: A solution of the pteridin-2,4,7-triones (**1**) (200 mg) in alcohol (70 ml) under an oxygen atmosphere in the presence of a sensitizer under the same conditions as described above for 1-2 h. An usual work-up gave the corresponding endoperoxides (**4,5**).

6-Phenyl-1,3,8-trimethyl-5'-methoxypteridin-2,4,7-trione 6,8'-Endoperoxide (4a); m.p. 169-171 °C; IR(KBr) 3320, 3290, 1715, 1675 cm^{-1}; $\delta_H(CDCl_3)$ 3.15 (3H, s), 3.18 (3H, s), 3.24 (3H, s), 3.25 (3H, s), 4.56 (1H, br s), 7.35-7.60 (5H, m); $\delta_C(CDCl_3)$ 28.6(q), 32.4(q), 33.2(q), 49.6(q), 81.8(s), 89.8(s), 97.3(s), 126.6(d), 128.2(d), 130.0(d), 130.6(d), 152.2(s), 164.8(s), 167.4(s); m/z(CI) 363 ($M^+ + 1$). (Anal. Calcd. for $C_{16}H_{18}N_4O_6$: C, 53.03; H, 5.00; N, 15.46. Found: C, 52.92; H, 4.97; N, 15.34%).

1,3,6,8-Tetramethyl-5'-methoxypteridin-2,4,7-trione 6,8'-Endoperoxide (4b); m.p. 149-151 °C; IR(KBr) 3310, 1715, 1680 cm^{-1}; $\delta_H(CDCl_3)$ 1.58 (3H,

s), 3.14 (6H, s), 3.15 (3H, s), 3.27 (3H, s), 4.27 (1H, br s); $\delta_C(CDCl_3)$ 16.1(q), 28.7(q), 32.1(q), 33.3(q), 49.5(q), 81.6(s), 87.9(s), 97.2(s), 152.4(s), 165.0(s), 167.7(s). (Anal. Calcd. for $C_{11}H_{16}N_4O_6$: C, 44.00; H, 5.37; N, 18.65. Found: C, 43.97; H, 5.37; N, 18.58%).

6,8-Dimethyl-1,3-diphenyl-5'-methoxypteridin-2,4,7-trione 6,8'-Endoperoxide (4c); m.p. 122-123 °C; IR(KBr) 3310, 1715, 1690 cm^{-1}; $\delta_H(CDCl_3)$ 1.57 (3H, s), 2.62 (3H, s), 3.30 (3H, s), 4.46 (1H, s), 7.15-7.67 (10H, m); $\delta_C(CDCl_3)$ 16.2(q), 32.5(q), 49.8(q), 82.1(s), 87.9(s), 97.8(s), 128.4(d), 128.9(d), 129.3(d), 129.4(d), 134.2(s), 136.2(s), 150.9(s), 165.0(s), 167.3(s); m/z(CI) 425 ($M^+ + 1$).

8-Methyl-1,3,6-triphenyl-5'-methoxypteridin-2,4,7-trione 6,8'-Endoperoxide (4d); IR($CHCl_3$) 3210, 1705, 1670, 1620 cm^{-1}; $\delta_H(CDCl_3)$ 3.12 (3H, s), 3.93 (3H, s), 4.87 (1H, br s), 6.93-7.49 (11H, m), 7.62-7.80 (4H, m); $\delta_C(CDCl_3)$ 27.9(q), 52.4(q), 87.4(s), 102.5(s), 116.7(d), 125.1(d), 125.3(d), 125.8(d), 127.8(d), 128.3(d), 129.1(d), 129.2(d), 129.5(d), 130.2(d), 133.7(s), 135.9(s), 156.4(s), 160.4(s), 160.6(s).

1,3-Diphenyl-6,8-dimethyl-5'-ethoxypteridin-2,4,7-trione 6,8'-endoperoxide (5c); IR($CHCl_3$) 3320, 1740, 1700 cm^{-1}; $\delta_H(CDCl_3)$ 1.19 (3H, t, J=7.0 Hz), 1.58 (3H, s), 2.64 (3H, s), 3.21-3.53 (1H, m), 3.66-3.97 (1H, m), 4.45 (1H, br s), 7.08-7.73 (10H, m); $\delta_C(CDCl_3)$ 15.3(q), 16.3(q), 32.6(q), 58.1(t), 81.7(s), 87.8(s), 97.8(s), 128.3(d), 128.9(d), 129.1(d), 129.3(d), 134.2(s), 136.1(s), 150.9(s), 165.4(s), 167.3(s); m/z(CI) 439 ($M^+ + 1$).

Thermal Reactions of 6-Phenyl-1,3,8-trimethylpteridin-2,4,7-trione 6,8'-Endoperoxide (2a): (a) In dichloromethane: A solution of **2a** (100 mg) in dichloromethane (30 ml) was heated to reflux for 3 h under argon. An usual work-up yielded 6-phenyl-1,3,8-trimethylpteridin-2,4,7-trione (**1a**) quantitatively. (b) In methanol-dichloromethane: A solution of **2a** (100 mg) in methanol-dichloromethane (2:3) (30 ml) was refluxed for 3 h under argon and an usual work-up gave 6-phenyl-1,3,8-trimethyl-5'-methoxypteridin-2,4,7-trione 6,8'-endoperoxide (**4a**) in almost quantitative yield.

Photochemical Reactions of 6-Phenyl-1,3,8-trimethylpteridin-2,4,7-trione 6,8'-Endoperoxide (2a): (a) in dichloromethane: A solution of **2a** (100 mg) in dichloromethane (70 ml) was irradiated in a Pyrex vessel with a high-pressure mercury lamp under argon for 6 h at room temperature. After evaporation of the solvent in vacuo, the residue was purified with a silica gel column chromatography to give **1a** in almost quantitative yield. (b) In methanol-dichloromethane: A solution of **2a** (100 mg) in methanol-dichloromethane (2:3) (50 ml) was irradiated under the same conditions as described above for 6 h and an usual work-up gave **4a** quantitatively.

Photochemical Reactions of the 5'-Methoxypteridin-2,4,7-trione 6,8'-Endoperoxides (4a,b): A solution of the 5'-methoxypteridin-2,4,7-trione

6,8'-endoperoxide (**4**) (100 mg) in methanol (70 ml) was irradiated in a Pyrex vessel with a high-pressure mercury lamp under argon for 10-24 h at room temperature. After removal of the solvent, the residue was chromatographed on a silica gel column with benzene-ethyl acetate (1:9) to give the barbituric acid derivatives (**6**).

1,3-Dimethyl-5-benzoylamino-5-methoxybarbituric Acid (6a). 169-171 °C; IR(KBr) 3220, 1700, 1685, 1640 cm^{-1}; $\delta_H(CDCl_3)$ 3.39 (6H, s), 3.41 (3H, s), 7.24-7.50 (3H, m), 7.69-7.79 (2H, m), 7.95 (1H, br s); $\delta_C(CDCl_3)$ 29.2(q), 54.1(q), 81.5(s), 127.6(d), 128.4(d), 131.0(s), 132.7(d), 150.2(s), 165.4(s), 168.8(s); m/z(CI) 306 ($M^+ + 1$). (Anal. Calcd. for $C_{14}H_{15}N_3O_5$: C, 55.08; H, 4.95; N, 13.76. Found: C, 55.05; H, 4.98; N, 13.65%).

1,3-Dimethyl-5-acetylamino-5-methoxybarbituric Acid (6b); m.p. >250 °C; IR(KBr) 3315, 1700(sh), 1690, 1665(sh) cm^{-1}; $\delta_H(CDCl)$ 2.00 (3H, s), 3.37 (6H, s), 3.43 (3H, s), 7.96 (1H, br s); $\delta_C(CDCl_3)$ 21.6(q), 29.2(q), 54.0(q), 80.9(s), 150.0(s), 165.5(s), 172.2(s). (Anal. Calcd. for $C_9H_{13}N_3O_5$: C, 44.44; H, 5.39; N, 17.28. Found: C, 44.38; H, 5.42; N, 17.17%).

Dye-sensitized Photooxygenation of 1,3,6,8-Tetramethylpteridin-2,4,7-trione (1b) in the Presence of DABCO: An oxygenated solution of **1b** (200 mg) in methanol (70 ml) in the presence of methylene blue (ca 2 mg) as a sensitizer and 1,4-diazabicyclo[2.2.2]-octane (DABCO) (480 mg) as a singlet oxygen quencher was irradiated in a Pyrex vessel with a halogen lamp for 2 h at room temperature. An usual work-up as described above gave 1,3,6,8-tetramethyl-5'-methoxypteridin-2,4,7-trione 6,8'-endoperoxide (**4b**) in 38% yield and the starting material (**1b**).

Thermal Reactions of 6-Phenyl-1,3,8-trimethylpteridin-2,4,7-trione 6,8'-Endoperoxide (2a) in the Presence of Singlet Oxygen Acceptors (7-12): A solution of the endoperoxide (**2a**) (200 mg, 0.6 mmol) and singlet oxygen acceptors (**7-12**) (0.6-0.06 mmol) in dichloromethane (30 ml) was refluxed under an argon atmosphere for 4-8 h. After removal of the solvent, the residue was chromatographed on a silica gel column with benzene-ethyl acetate (benzene only-4:1) or methanol-ethyl acetate (1:4) to yield the corresponding oxidized products (**13-18**) and 6-phenyl-1,3,8-trimethylpteridin-2,4,7-trione (**1a**). In the case of tetraphenylfuran (**8**), the reaction was carried out in aqueous dichloromethane to enhance the production of the epoxide (**13**). The oxidized products (**13-18**) thus obtained were confirmed by direct comparison of their IR and NMR spectra with those of authentic materials, which were independently prepared by the dye-sensitized photooxygenation of **7-12**.[7,15-18,19a,c]

Thermal Reaction of 6-Phenyl-1,3,8-trimethylpteridin-2,4,7-trione 6,8'-Endoperoxide (2a) with Tetraphenylfuran (7) in the Presence of DABCO: A solution of **2a** (330 mg, 1 mmol), tetraphenylfuran (**7**) (1 mmol), and

DABCO (1 mmol) in dichloromethane (75 ml) was heated to reflux under argon for 10 h. An usual work-up gave the epoxide (**13**) and the pteridin-2,4,7-trione (**1a**) in 26% and quantitative yields, respectively.

Thermal Reaction of 6-Phenyl-1,3,8-trimethylpteridin-2,4,7-trione 6,8'-Endoperoxide (2a) with Tetraphenylfuran (7) in the Presence of 2,6-Di-tert-butylphenol: A solution of the endoperoxide (**2a**) (50 mg, 0.15 mmol) and tetraphenylfuran (**7**) (0.15 mmol) in dichloromethane (75 ml) was heated to reflux under argon in the presence of 2,6-di-tert-butylphenol (1.5 mmol) as a free radical inhibitor for 4 h. An usual work-up gave the epoxide (**13**) and the pteridin-2,4,7-trione (**1a**) in 26% and quantitative yields, respectively.

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