Tetrahedron Vol. 25, pp 549 to 556 Pergamon Press 1969 Printed in Great Britain

PHOTOINDUCED REACTIONS—XXV

A ZWITTERIONIC PEROXIDE INTERMEDIATE IN THE PHOTOSENSITIZED OXYGENATION OF FULLY N-ALKYLATED URIC ACIDS[1,2]

T. MATSUURA and I. SAITO

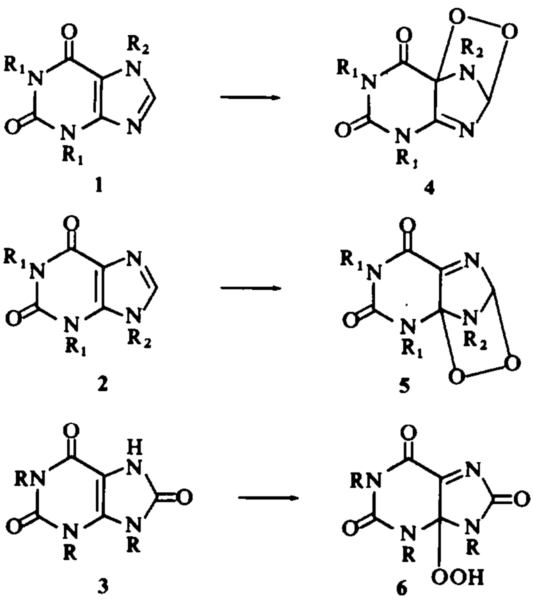
Department of Synthetic Chemistry, Faculty of Engineering,
Kyoto University, Kyoto, Japan

(*Received in Japan* 24 *July* 1968; *Received in the UK for publication* 23 *August* 1968)

Abstract—Photosensitized oxygenation of 1,3,7,9-tetramethyluric acid (**7a**) in methanol containing rose bengal as sensitizer yielded 4,5-dimethoxy-1,3,7,9-tetramethyluric acid (**10**) as the major product besides a small amount of allocaffeic acid (**11**). When photosensitized oxygenation was carried out in chloroform in the presence of methylene blue, **7a** gave 1,3,7-trimethylcaffolide (**12a**) and 1,3-dimethylparabanic acid (**13**). Under the same conditions, 1-ethyl-3,7,9-trimethyluric acid (**7b**) afforded **12b**, **13**, and **14b** and 9-ethyl-1,3,7-trimethyluric acid (**7c**) gave **12c** and **14c**. Mechanisms involving an initial attack of singlet oxygen to **7** forming a zwitterionic peroxide are proposed.

IN PREVIOUS papers,[1,3,4] the photosensitized oxygenation of various types of hydroxylated purine derivatives leading to degradation products has been described. It has been shown that, in the case of 2,6-dihydroxypurine derivatives such as **1**, **2**, and **3**, the initial attack of oxygen, possibly excited singlet oxygen, occurs at double bonds of the imidazole moiety to form a peroxide intermediate which could account for the formation of the degradation products. We have formulated two types of peroxide intermediates. When two double bonds are present in the imidazole moiety as in **1** and **2**, an *endo*-peroxide as **4** and **5** may be the intermediate. It is generally accepted that such an *endo*-peroxide is an intermediate in the photosensitized oxygenation of cyclic dienes[5] and also of certain N-heterocycles[6,7] bearing a —C=N—C=C— group. On the other hand, when a —C=C—NH— group is present in the imidazole moiety as in **3**, a hydroperoxide as **6** may be formed and accompanied by migration of the double bond. This type of hydroperoxide is also generally accepted as an intermediate in the photooxygenation of various N-heterocycles such as imidazoles,[7] pyrroles,[8] and indoles.[9]

The latter type of peroxide is well known as an initial product in the photooxygenation of simple olefins bearing an allylic hydrogen; namely $\text{—}\overset{|}{\text{C}}\text{=}\overset{|}{\text{C}}\text{—}\overset{|}{\text{C}}\text{H—} \rightarrow \text{—}\overset{|}{\text{C}}\text{(OOH)—}\overset{|}{\text{C}}\text{=}\overset{|}{\text{C}}\text{—}$. To the best of our knowledge the photosensitized oxygenation of olefins having no allylic hydrogen has not been reported, although some compounds having a vinyl ether group, —C=C—O—R, without having any allylic

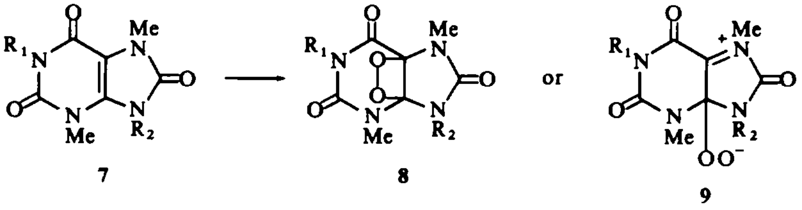


1 → 4

2 → 5

3 → 6

hydrogen undergo photooxidative cleavage of C=C double bond.[10,*] It appeared, therefore, interesting to investigate photosensitized oxygenation of fully N-alkylated uric acids (**7**) which in contrast to **3** have no NH group. A compound such as **7** may form a 4-membered cyclic peroxice (**8**) or a zwitterionic peroxide (**9**).

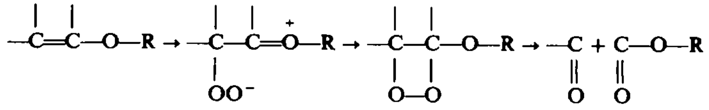


7 → 8 or 9

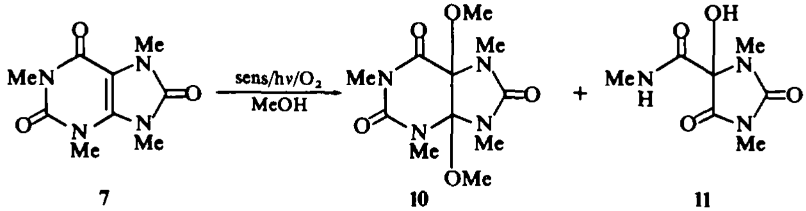
When a methanol solution of 1,3,7,9-tetramethyluric acid (**7a**) was submitted to photosensitized oxygenation in the presence of rose bengal, 0·63 mole of oxygen was consumed rapidly and 4,5-dimethoxy-1,3,7,9-tetramethyluric acid (**10**) and allocaffeic acid (**11**) were obtained in 35 and 5% yield, respectively. Both products were identified by independent syntheses.[11,12] Allocaffeic acid (**11**) probably was formed by hydrolysis of **10** during chromatographic separation of the products. In fact, **10** is easily hydrolyzed by acid treatment to give **11**.[12]

---

[*] It has been proposed that cleavage of C=C double bond proceeds *via* a four-membered cyclic peroxide intermediate.[10b] However, a zwitterionic peroxide intermediate may also account for the cleavage reaction (see below) as follows.



$$-\overset{|}{C}=\overset{|}{C}-O-R \rightarrow -\underset{OO^-}{\overset{|}{\underset{|}{C}}}-\overset{|}{C}=\overset{+}{O}-R \rightarrow -\underset{O-}{\overset{|}{\underset{|}{C}}}-\underset{-O}{\overset{|}{\underset{|}{C}}}-O-R \rightarrow -\underset{O}{\underset{\|}{C}} + \underset{O}{\underset{\|}{C}}-O-R$$

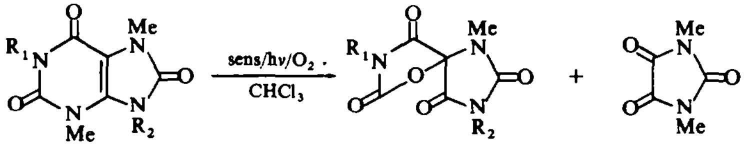


7 10 11

On the other hand, when photosensitized oxygenation was carried out in chloroform using methylene blue as sensitizer, fully N-alkylated uric acids (**7**) gave different types of products. Thus, 1,3,7,9-tetramethyluric acid (**7a**) afforded, after absorption of 0·59 mole of oxygen at a slower rate than in methanol, 1,3,7-trimethylcaffolide (**12a**)[12] and 1,3-dimethylparabanic acid (**13**) in 42 and 7% yield, respectively. Both compounds were identified by a direct comparison with authentic specimens.

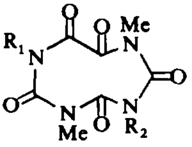
Under similar conditions, 1-ethyl-3,7,9-trimethyluric acid (**7b**) absorbed 0·72 mole of oxygen in chloroform to yield 1,3-dimethyl-7-ethyl-caffolide (**12b**),[13] 1,3-dimethylparabanic acid (**13**), and an oxygen adduct $C_{10}H_{14}N_4O_5$ in 12, 8, and 22% yields, respectively. The structure of **12b** was confirmed by its synthesis and by hydrolysis to 1,3-dimethyl-5-hydroxyhydantoin-5-N-ethylcarboxyamide.[13] The molecular formula for the adduct was confirmed by the appearance of a parent peak at *m/e* 270. The IR spectrum shows a broad carbonyl absorption band at 1750–1650 cm^{-1} but neither NH or OH bands. The NMR spectrum exhibits three singlets at τ 6·85, 7·01, and 7·10 corresponding to three N-Me groups, a quartet at τ 6·32 ($J = 7$ c/s), and a triplet at τ 8·87 ($J = 7$ c/s). The latter two signals were assigned to an N–Et group. Hydrolysis of the adduct with boiling water afforded 1,3-dimethyl- and 1-ethyl-3-methylparabanic acids in 67 and 26% yields, respectively. The above results support structure **14b** for this compound.

Photosensitized oxygenation of 9-ethyl-1,3,7-trimethyluric acid (**7c**) in chloroform yielded 1,7-dimethyl-3-ethylcaffolide (**12c**) and an oxygen adduct (**14c**) in 5 and 16% yields, respectively, after absorption of 0·64 mole of oxygen. The former product was identified by direct comparison with an authentic sample.[14] The spectral data of the oxygen adduct corresponds to those of the adduct **14b**, and structure **14c** was given.



7a, b, c **12a, b, c** **13**

a: $R_1 = R_2 = Me$
b: $R_1 = Et, R_2 = Me$
c: $R_1 = Me, R_2 = Et$

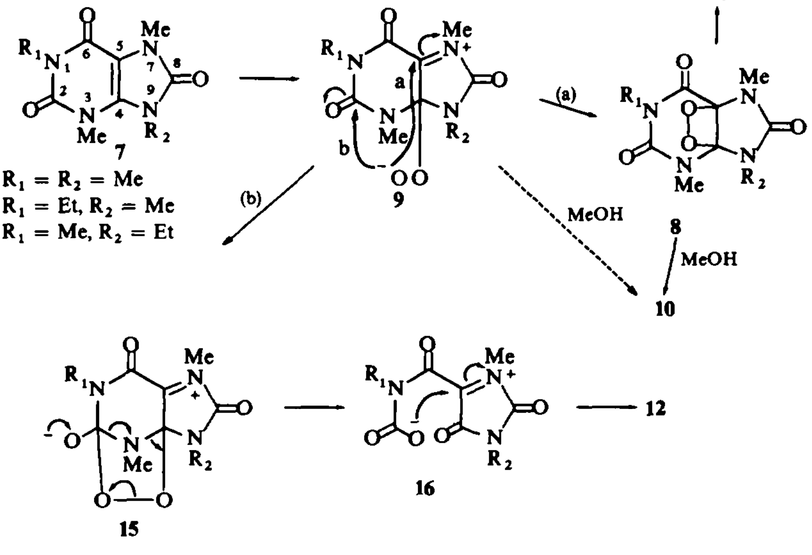


14b, c

Although the formation of 4,5-dimethoxy-1,3,7,9-tetramethyluric acid (**10**) from **7a** appears analogous to the conversion of 1,3-dimethyl-9-phenyluric acids (**3**) to the corresponding 4,5-dimethoxyuric acid derivatives, previously reported,[1] the hydroperoxide intermediate such as **6** cannot account for the transformation of **7a** into **10** because of the lack of a C=C—NH group as in **3**. We, therefore, propose a zwitterionic peroxide **9a** for the first step intermediate in the photosensitized oxygenation of **7a**. As was discussed above, the 4-membered cyclic peroxide **8a** could also account for the formation of **10**. However, the results obtained in the photosensitized oxygenation of **7a**, **7b**, and **7c** in chloroform strongly support the initial formation of the zwitterionic peroxide **9**. The transformation of **7** into 1,3,7-trialkylcaffolides **12** clearly indicates that the 3-N-Me group was expelled during formation of **12**.

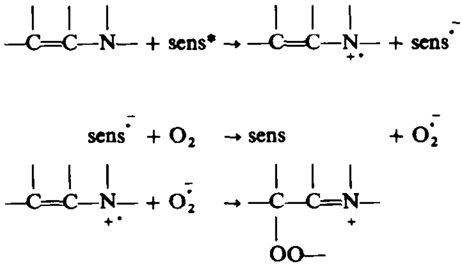
The decomposition of the zwitterionic peroxide **9** depends on conditions. As shown in Scheme 1, **9** could rearrange to the cyclic peroxide **8** (path a) which, in the presence of methanol, undergoes reductive cleavage to form the dimethoxyuric acid **10**.[1] An alternative route, by which the zwitterion **9a** is reductively solvolyzed with methanol at the 4-position accompanied by addition of methanol to the C=N bond, can also be considered. 4,5-Bond fission leading to the medium ring compounds **14b** and **14c** may occur either from **8** stepwise *via* **9** or directly from **9** by a concerted process. Finally, the formation of caffolides **12** can be rationalized only by the zwitterionic intermediate **9**. A cyclic tautomer **15**, which results from a nucleophilic attack of the perhydroxy anion on a carbonyl carbon at 2-position (path b), could lose a 3-N-Me group to form an intermediate **16** which in turn cyclizes to **12**. The loss of the 3-N-Me group corresponds to the photosensitized oxygenation of 1,3-diphenyl-2-methylisoindole leading to *o*-dibenzoylbenzene.[15] Zwitterionic peroxide such as **9** have been proposed by Foote *et al.*[16] and Wasserman *et al.*[17] as intermediates of the photosensitized oxygenation of a number of fully N-substituted enamines.

SCHEME 1



Evidence for the participation of singlet oxygen in dye-sensitized photooxygenation has been provided by various workers.[18–21] In order to elucidate whether singlet oxygen is involved in the photosensitized oxygenation of **7a**, **7b**, and **7c**, reaction of **7a** and **7b** with singlet oxygen, generated by non-photochemical means, was investigated. Reaction of **7a** with hydrogen peroxide and hypochlorite in aqueous methanol[18] afforded 4,5-dimethoxy-1,3,7,9-tetramethyluric acid (**10**) and 1,3-dimethylparabanic acid (**13**) in 2 and 38% yield, respectively. The latter product seems to be formed by hydrolytic decomposition of **10**. In control experiments, **7a** did not react with hydrogen peroxide alone, but it was decomposed by hypochlorite in aqueous methanol to give various products among which **10** and **13** could not be detected. Reaction of **7b** with 9,10-diphenylanthracene peroxide in boiling chloroform[19] gave, in addition to recovery of considerable starting material, only a trace of 1,3-dimethyl-7-ethylcaffolide (**12b**) which was detected by TLC on silica gel. On the other hand, when **7a** was treated with an excess triphenyl phosphite-ozone adduct at $-30°$,[20] 1,3,7-trimethylcaffolide (**12a**) was obtained in 5% yield.

The above results indicate that the zwitterionic peroxides (**9**) may be formed at least in part by the attack of singlet oxygen on the tetraalkyluric acids (**7**) in the photosensitized oxygenation. An alternative pathway involving an electron transfer from a substrate to the triplet excited sensitizer may also account for the formation of the zwitterionic peroxide, according to the equations: Such an electron transfer mechanism has been postulated by Morita and Kato from the flash photolysis



$$-\overset{|}{C}=\overset{|}{C}-\overset{|}{N}- + \text{sens}^* \rightarrow -\overset{|}{C}=\overset{|}{C}-\underset{+\cdot}{\overset{|}{N}}- + \text{sens}^{\overset{-}{\cdot}}$$

$$\text{sens}^{\overset{-}{\cdot}} + O_2 \rightarrow \text{sens} + O_2^{\overset{-}{\cdot}}$$

$$-\overset{|}{C}=\overset{|}{C}-\underset{+\cdot}{\overset{|}{N}}- + O_2^{\overset{-}{\cdot}} \rightarrow -\underset{\underset{OO-}{|}}{\overset{|}{C}}-\overset{|}{C}=\underset{+}{\overset{|}{N}}-$$

experiments on guanine in the presence of thionine.[22] Although, from the available data, we cannot rigorously distinguish between these two mechanisms for the formation of the zwitterionic peroxide, the direct attack of singlet oxygen appears to be more favourable in view of previous reports on the electrophillic properties of singlet oxygen.[23,24]

EXPERIMENTAL

Photosensitized Oxygenation of 1,3,7,9-*tetramethyluric acid* (**7a**).

A. *In methanol.* A soln of **7a**[25] (2·0 g, 8·90 mmoles) in a mixture of abs MeOH (100 ml) and $CHCl_3$ (5 ml) containing rose bengal (20 mg) was irradiated by a tungsten lamp for 1 hr as described previously,[1] until O_2 (140 ml, 5·6 mmoles) was consumed. The mixture was evaporated and the residue was chromatographed on a silica gel column (40 g). Elution with $CHCl_3$ (ca. 100 ml) yielded **10** as a crystalline solid (0·87 g, 35%). Recrystallization from acetone gave crystals, m.p. 127–128° (lit.[11], m.p. 133°), which were identical with an authentic sample prepared according to the method of Blitz *et al.*[11] (by IR); ν_{max}^{Nujol} 1730 and 1680 cm^{-1}; NMR ($CDCl_3$), τ, 6·61, 6·68, 6·80, 6·98, 7·10, and 7·21 (all singlets, >N—Me and —OMe).

Further elution with $CHCl_3$–acetone (97:3) gave **11** as a semisolid (85 mg, 5%). Recrystallization from EtOAc gave crystals, m.p. 170° (lit.,[12] m.p. 168–169°). The compound was identical with the authentic sample prepared according to the method of Blitz[12] (by IR); ν_{max}^{Nujol} 1790, 1730, and 1665 cm^{-1}; NMR (DMSO-d_6), τ 1·80 (s*, 1H, NH), 2·42 (s, 1H, OH), 7·41 (s, 3H, >N—Me), 7·45 (d (J = 5 c/s), 3H, —NH—Me), 7·18 (s, 3H, >N—Me).

---

* s = singlet, d = doublet etc.

When a 100 W high-press mercury lamp through a Pyrex filter was used in the photosensitized oxygenation, the results were virtually the same as above.

B. *In* $CHCl_3$. A soln of **7a** (2·0 g, 8·90 mmoles) in $CHCl_3$ (100 ml) containing methylene blue (50 mg) was irradiated by a 100 W high-press mercury lamp for 4 hr, until O_2 (130 ml, 5·2 mmoles) was consumed. After removal of the solvent, the residue was chromatographed on a silica gel column (40 g). Elution with $CHCl_3$ (ca. 300 ml) gave **12a** as a crystalline solid (0·85 g, 42%). Recrystallization from EtOH yielded crystals, m.p. 207–208° (lit.[12], m.p. 205°), which were identical with the authentic specimen prepared according to the procedure of Blitz[12] (by IR); ν_{max}^{Nujol} 1800, 1760–1690 cm^{-1}; NMR ($CDCl_3$), τ 6·84 (s, 3H, >N—Me), 6·96 (s, 3H, >N—Me), 7·14 (s, 3H, >N—Me).

Further elution with $CHCl_3$ gave **13** (95 mg, 7%), identified by IR.

Photosensitized oxygenation of 1-*ethyl*-3,7,9-*trimethyluric acid* (**7b**)

A soln of **7b**[13] (2·0 g, 8·4 mmoles) and methylene blue (50 mg) in $CHCl_3$ (100 ml) was irradiated by a 100 W high-pressure mercury lamp for 2·5 hr, until O_2 (150 ml, 6·0 mmoles) was consumed. After removal of the solvent, the residue was chromatographed on a silica gel column (30 g). Elution with $CHCl_3$ (100 ml) gave **14b** as a crystalline solid (0·51 g, 22%). Recrystallization from acetone gave crystals, m.p. 101–103°; ε_{210}^{EtOH} 37,200; ν_{max}^{Nujol} 1750–1710, 1670 cm^{-1}; mass spectrum (*m/e*), 270 (parent peak), 241, 226, 212, 196, 185, 170, 156, 143 (base peak). (Found: C, 44·27; H, 5·15; N, 20·15. $C_{10}H_{14}N_4O_5$ requires: C, 44·44; H, 5·22; N, 20·73%).

Elution with $CHCl_3$ (250 ml) yielded **12b** (0·22 g, 12%). Recrystallization from EtOH gave crystals, m.p. 95–96° (lit.[13], m.p. 93°), which were identical with the authentic sample prepared according to the method of Blitz *et al.*[13] (by mixture m.p. and IR); ν_{max}^{Nujol} 1800, 1730 cm^{-1}; NMR ($CDCl_3$), τ 6·98 (s, 3H, >N—Me), 7·16 (s, 3H, >N—Me), 6·39 (qu (J = 7 c/s), 2H, >N—CH_2—Me), 8·71 (tr (J = 7 c/s), 3H, >N—CH_2—Me).

Elution with $CHCl_3$ (400 ml) gave **13** (0·11 g, 8%), identified by IR.

Hydrolysis of **14b**. A suspension of **14b** (50 mg) in H_2O (5 ml) was boiled for 3 hr. After removal of the water *in vacuo*, the residue was extracted with acetone (5 ml). The extract was purified by preparative TLC on solica gel plates using $CHCl_3$–EtOH (20:1) as a solvent. Bands of R_f 0·70 and R_f 0·50 were cut off and then extracted with acetone. From the band of R_f 0·70, 1-ethyl-3-methylparabanic acid (5 mg, 26%), m.p. 47–48° (lit.,[26] m.p. 44°), was obtained. 1,3-Dimethylparabanic acid (18 mg, 67%) was obtained from the band of R_f 0·50. Both compounds were identified by IR.

Hydrolysis of 1,3-*dimethyl*-7-*ethylcaffolide* (**12b**) *to* 1,3-*dimethyl*-5-*hydroxyhydantoin*-5-N-*ethylcarboxyamide*. Compound **12b** was hydrolysed according to the method of Biltz and Max.[13] A suspension of **12b** (0·5 g) in H_2O (15 ml) was boiled for 30 min. After removal of the water, the residue was recrystallized from EtOAc to give 1,3-dimethyl-5-hydroxyhydantoin-5-N-ethylcarboxyamide (0·21 g, 68%), m.p. 156–157·5° (lit.,[13] m.p. 153°); ν_{max}^{Nujol} 1780, 1710, 1650 cm^{-1}; NMR ($CDCl_3$), τ 2·94 (s, 1H, NH) 3·93 (s, 1H, OH) 7·11 (s, 3H, >N—Me), 7·27 (s, 3H, >N—Me), 6·71 (qu-d (J = 7 c/s, J = 4 c/s) 2H, —NH—CH_2—Me), 8·85 (tr (J = 7 c/s), 3H, —NH—CH_2—Me).

Photosensitized oxygenation of 9-*ethyl*-1,2,7-*trimethyluric acid* (**7c**)

A soln of **7c**[25] (2·0 g, 8·4 mmoles) in $CHCl_3$ (100 ml) containing methylene blue (50 mg) was photooxidized as described above for 12 hr, until O_2 (135 ml, 5·4 mmoles) was consumed. After removal of the solvent, the residue was chromatographed on a silica gel column (40 g). Elution with $CHCl_3$ (150 ml) gave **14c** as a crystalline solid (0·21 g, 16%). Recrystallization from acetone yielded crystals, m.p. 94–95°, ε_{210}^{EtOH} 38,100; ν_{max}^{Nujol} 1740–1700, 1660 cm^{-1}; NMR ($CDCl_3$), τ 6·80 (s, 3H, >N—Me), 6·86 (s, 3H, >N—Me), 6·96 (s, 3H, >N—Me), 6·54 (qu (J = 7 c/s), 2H, >N—CH_2—Me), 8·96 (tr (J = 7 c/s), 3H >N—CH_2—Me); mass spectrum (*m/e*), 270 (parent peak). (Found: C, 44·39; H, 5·39; N, 20·28. $C_{10}H_{14}N_4O_5$ requires: C, 44·44; H, 5·22; N, 20·73%).

Further elution with $CHCl_3$ (300 ml) gave **12c** (50 mg, 5%). Recrystallization from EtOH gave crystals, m.p. 103–105° (lit.,[14] m.p. 102°), which were identical with the authentic sample prepared according to the method of Biltz *et al*[14]; ν_{max}^{Nujol} 1800, 1750–1700 cm^{-1}; NMR ($CDCl_3$), τ 6·88 (s, 3H, $>$N—Me), 7·17 (s, 3H, $>$N—Me), 6·47 (qu (J = 7 c/s), 2H, $>$N—CH_2—Me), 8·78 (tr (J = 7 c/s), 3H, $>$N—CH_2—Me).

Further elution with $CHCl_3$ (500 ml) gave the starting material (**7c**) (0·85 g, 42%).

Oxidation of **7a** *and* **7b** *with singlet oxygen from various sources*

A. *From hydrogen peroxide and hypochlorite.* The reaction was carried out according to the procedure of Foote *et al.*[18] A soln of **7a** (1·0 g, 4·45 mmoles) in MeOH (300 ml) was cooled on an ice-bath, and 30% H_2O_2 (5 ml, 45 mmoles) was added. To the mixture 9% NaOClaq (28 ml, 33 mmoles) was added dropwise under stirring in a period of 1 hr. The reaction mixture (pH 8·9) was diluted with H_2O (500 ml) and extracted with $CHCl_3$ (500 ml). The extract was chromatographed on a silica gel column (20 g). Elution with $CHCl_3$ gave **13** (60 mg, 38%), **10** (5 mg, 2%) and the unreacted **7a** (0·75 g, 75% recovery). These products were identified by IR.

To a soln of **7a** (100 mg) in MeOH (30 ml) 30% H_2O_2 (0·5 ml) was added at room temp, and the reaction mixture was stirred for 1 hr. The starting material **7a** was recovered quantitatively.

To a soln of **7a** (100 mg) in MeOH (30 ml) 9% NaOClaq (3 ml) was added as described above. The reaction mixture was found by TLC to consist of the unreacted **7a** and three unidentified compounds, among which **10** and **13** could not be detected.

B. *From 9,10-diphenylanthracene peroxide.* The reaction was carried out according to the procedure of Wasserman *et al.*[19] A soln of **7b** (100 mg, 0·42 mmoles) and 9,10-dephenylanthracene peroxide (300 mg, 0·83 mmole) in $CHCl_3$ (20 ml) was boiled for 3 days. A TLC analysis (silica gel, $CHCl_3$—EtOH (20:1)) of the reaction mixture showed the presence of a trace of **12b** and over 90% of the starting material **7b**.

C. *From the triphenyl phosphite–ozone adduct.* According to the procedure of Thompson[27] and Kaplan,[20] the triphenyl phosphite-ozone adduct was prepared from triphenyl phosphite (6·0 g, 17·0 mmoles) in CH_2Cl_2 (200 ml). To the soln a cold soln of **7a** (2·0 g, 8·9 mmoles) in CH_2Cl_2 (50 ml) was added, and the reaction mixture was allowed to warm slowly to −30° in a period of 8 hr and then to room temp. The mixture was found by TLC to consist of at least 6 compounds along with triphenyl phosphate. After removal of the solvent, the residue was chromatographed on a silica gel column (65 g). Elution with $CHCl_3$ (150 ml) yielded triphenyl phosphate (5·3 g, 85%). Further elution with $CHCl_3$ (500 ml) gave **12a** (85 mg, 5% based on the reacted **7a**). Recrystallization from EtOH gave crystals, m.p. 205–207°, which were identical with the authentic sample described above (by IR). Elution with $CHCl_3$ (600 ml) yielded the unreacted **7a** (0·18 g, 9% recovery). Acetone eluted red brown polymers (0·88 g).

REFERENCES

[1] Part XXIV, T. Matsuura and I. Saito, *Tetrahedron* **24**, 541 (1968).

[2] This work was preliminary communicated in, T. Matsuura and I. Saito, *Tetrahedron Letters* 3273 (1968).

[3] T. Matsuura and I. Saito, *Chem. Comm.* 693 (1967).

[4] T. Matsuura and I. Saito, *Tetrahedron* **24**, 6609 (1968).

[5] K. Gollnick and G. O. Schenck, *1,4-Cycloaddition* (Edited by J. Hamer) p. 255. Academic Press, New York (1967).

[6] H. H. Wasserman and E. Druckrey, *J. Am. Chem. Soc.* **90**, 2440 (1968).

[7] E. H. White and M. J. C. Harding, *Photochem. Photobiol.* **4**, 1124 (1965).

[8] G. Rio, A. Ranjon and O. Pouchot, *C.R. Acad. Sci., Paris* **263**, 634 (1966).

[9] Z. Yoshida and M. Kato, *J. Am. Chem. Soc.* **76**, 311 (1954); *J. Chem. Soc. Japan* **75**, 112 (1954).

[10] [a] T. Kubota, N. Ichikawa, K. Matsuo and K. Shibata, *Tetrahedron Letters* 4671 (1966);
[b] H. Sakuragi, K. Tokumaru and O. Shimomura, *Symposium on Photochemistry, Tokyo*, Abstracts of Papers, p. 83. Nov. (1967).

[11] H. Biltz and P. Damm, *Liebigs Ann.* **413**, 186 (1917).

[12] H. Biltz, *Ber. Dtsch. Chem. Ges.* **43**, 1603 (1910).

[13] H. Biltz and F. Max, *Liebigs Ann.* **414**, 74 (1917).

[14] H. Biltz and M. Bergius, *Ibid.* **414**, 63 (1917).

[15] W. Theilacker and W. Schmidt, *Ibid.* **605**, 43 (1957).

[16] C. S. Foote and J. W. P. Lin, *Tetrahedron Letters* 3263 (1968).

[17] H. H. Wasserman, K. Stiller and M. B. Floyd, *Ibid.* 3277 (1968).

[18] C. S. Foote, S. Wexler, W. Ando and R. Higgins, *J. Am. Chem. Soc.* **90**, 975 (1968) and refces cited therein.

[19] H. H. Wasserman and J. R. Scheffet, *Ibid.* **89**, 3073 (1967).
[20] R. W. Murray and M. L. Kaplan, *Ibid.* **90**, 537 (1968).
[21] E. McKeon and W. A. Waters, *J. Chem. Soc.* (B), 1040 (1966).
[22] M. Morita and S. Kato, *Symposium on Photochemistry*, Osaka, Japan, Oct. (1966).
[23] K. R. Kopecky and H. J. Reich, *Canad. J. Chem.* **43**, 2265 (1965).
[24] R. Higgins, C. S. Foote, and H. Cheng, *International Oxidation Symposium* "Preprints", Vol. 2; p, 672. San Francisco, Sept. (1967).
[25] R. C. Huston and W. F. Allen, *J. Am. Chem. Soc.* **56**, 1358 (1934).
[26] R. Andreasch, *Ber. Dtsch. Chem. Ges.* **31**, 138 (1898).
[27] Q. E. Thompson, *J. Am. Chem. Soc.* **83**, 846 (1961).