Sensitized Photooxygenation of 9-Vinylphenanthrenes

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The sensitized photooxygenation of several 9-vinylphenanthrenes in carbon tetrachloride was investigated. In the cases of 9-vinyl- and 9-(β-substituted vinyl)phenanthrenes, the 1,4-cycloaddition of singlet oxygen to a conjugated system composed of the side chain and 9,10-double bond of the ring surpassed other oxidation modes, *i.e.*, the "ene" reaction and 1,2-cycloaddition of singlet oxygen, to give the 1,2-dioxatriphenylene-type peroxides. On the other hand, the sensitized photooxygenation of 9-isopropenylphenanthrene gave a hydroperoxide due to the "ene" reaction.

Anthracenes are known to easily undergo photooxygenation to give 9,10-epidioxides, while phenanthrenes have scarcely been reported to react with singlet oxygen.$^{1)}$ Recently, an aromatic double bond in conjugation with extranuclear unsaturation has observed to produce an active diene system capable of undergoing the 1,4-cycloaddition of singlet oxygen for certain 1,1-diphenylethylenes,$^{2)}$ cyclic styrene derivatives,$^{3)}$ vinylnaphthalenes,$^{4)}$ and some vinyl-substituted heteroaromatics.$^{5)}$ These facts promted us to investigate the sensitized photooxygenation of 9-vinylphenanthrenes. 9-Vinyl- and 9-(β-substituted vinyl)phenanthrenes, **1a**—**d**, underwent the 1,4-cycloaddition of singlet oxygen to give 1,2-dioxatriphenylene-type peroxides, **2a**—**d**, while 9-(α-substituted vinyl-) such as 9-isopropenylphenanthrene (**1e**) did not, although the "ene" reaction did occur.

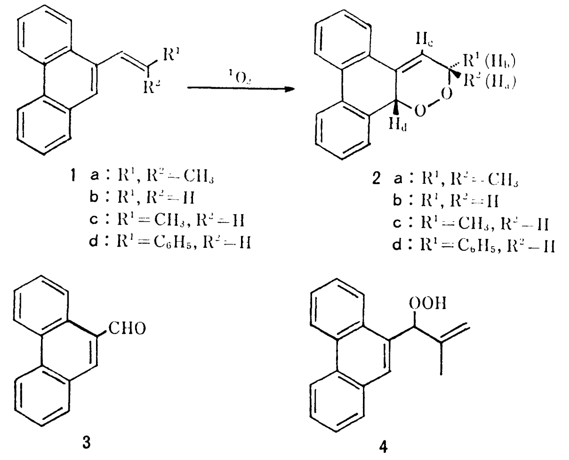

Fig. 1.

Results and Discussion

Preparation of 9-Vinylphenanthrenes. Phenanthrenes having 9-vinyl- (**1b**), 9-isopropenyl- (**1e**), and *trans*-9-styryl- (**1d**) substituents were prepared from 9-formylphenanthrene or 9-acetylphenanthrene using a Wittig reaction. The other phenanthrene, 9-(2-methyl-1-propenyl)- (**1a**) and *trans*-9-(1-propenyl)-phenanthrene (**1c**) were synthesized by dehydration of the corresponding alcohols prepared by a Grignard reaction of 9-bromophenanthrene. The preparations of these vinylphenanthrenes are described in detail in the experimental section.

Photooxygenation of 9-Vinylphenanthrene. First the sensitized photooxygenation of 9-(2-methyl-1-propenyl)-phenanthrene (**1a**) was examined, since **1a** is expected to be most favorable for the 1,4-cycloaddition of singlet oxygen of the phenanthrene **1a**—**e** in accord with the results of the sensitized photooxygenation of 1-vinylnaphthalenes.$^{5)}$ A solution of **1a** and tetraphenylporphine (TPP) as a sensitizer in carbon tetrachloride was irradiated externally with eight low-pressure sodium vapor lamps in an oxygen atmosphere at 5 °C. When the photolysate was chromatographed on silica gel, a peroxide, **2a**, was obtained in an 80% yield. The structure of **2a** was assigned on the basis of spectral evidence and combustion analysis. In this run, both 9-formylphenanthrene (**3**) and 9-(1-hydroperoxy-2-methyl-2-propenyl)phenanthrene (**4**) were scarcely detected. The former would be formed through the 1,2-addition of singlet oxygen to the side chain of **1a**, and the latter through "ene" reaction of **1a**. Similarly, irradiation of **1b** gave the corresponding endo peroxide, **2b** in a 40% yield. In this case, during the irradiation, a considerable amount of **1b** appeared to be polymerized.

Similar irradiation of *trans*-9-(1-propenyl)phenanthrene (**1c**) gave the corresponding endo peroxides, **2c**, in a 94% yield. The peroxide, **2c**, was one of two obtainable stereoisomers and its configuration was assigned by comparing the NMR spectra of **2a** and **2c** with those of the endo peroxides, **5**, derived from 1-(2-methyl-1-propenyl)-, *trans*-(1-propenyl)-, and *cis*-(1-propenyl)naphthalene.$^{5)}$ In the NMR spectra of peroxide **2**, the peak of the methyl attached to the carbon atom adjacent to the oxygen atom are situated at 1.29 and 1.42 ppm for **2a**, and at 1.39 ppm for **2c**, as shown in Table 1. On the other hand, in the cases of **5**, the corresponding quasi-axial and quasi-equatorial methyl peaks are located at 1.21—1.25 and 1.51 ppm, respectively.$^{5)}$ From these facts, **2c** was assigned to have the quasi-equatorial methyl. The sensitized photooxygenation of *trans*-9-styrylphenanthrene (**1d**) gave one of two possible isomeric 1,4-endo peroxides, **2d**, in a 63% yield. The structure of **2d** was also assigned by comparing its NMR spectrum with that

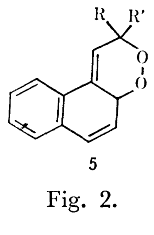

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Fig. 2.

Table 1. NMR spectral data of endo peroxides 2[a)]

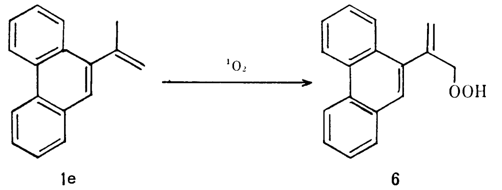
Chemical shifts (δ ppm)	H_a	H_b	H_c	H_d	R^1	R^2
2a	—	—	5.88	5.88	1.42[b)]	1.29[b)]
2b	5.12	5.37	5.99	5.99	—	—
2c	4.68	—	5.85	6.01	1.39[b)]	
2d	5.46	—	6.00	6.17	c)	—

Coupling constants (Hz)	J_{ab}	J_{ac}	J_{ad}	J_{bc}	J_{bd}	J_{cd}
2a	—	—	—	—	—	2.5
2b	17.0	3.0	3.5	3.0	3.0	?
2c	—	2.0	2.5	—	—	2.5
2d	—	3.5	3.5	—	—	2.5

a) Measured in CCl_4. b) R^1 and/or R^2=methyl. c) R^2=phenyl: 7.00—7.50 ppm.

of the endo peroxide of *trans*-1-styrylnaphthalene.[5)] Thus, the 1,4-cycloaddition of singlet oxygen to 9-vinylphenanthrenes **1** was confirmed to be stereospecific and the attack of singlet oxygen on the diene system may occur suprafacially. All the endo peroxides **2** obtained in this work were thermally stable and exhibited complex NMR spectra, which were analyzed using the spin-decoupling technique, as shown in Table 1.

For the sensitized photooxygenation of 1-vinylnaphthalenes, the α-substituent on the side chain was found to inhibit the 1,4-cycloaddition of singlet oxygen to the aromatic-extranuclear unsaturation system. This tendency was observed in the reaction of 9-vinylphenanthrene; when 9-isopropenylphenanthrene (**1e**) was oxygenated in a manner similar to that described above, no corresponding endo peroxide, **2**, but instead 9-(3-hydroperoxy-1-propen-2-yl)phenanthrene, (**6**), was formed. This result is in contradiction to the Diels-Alder reaction of maleic anhydride with **2e** in boiling xylene.[6)] One of the reasons for this phenomenon may be the steric repulsion between the α-methyl and a hydrogen atom at the 8-position of the aromatic ring, which may be overcome at high temperature.



1e 6

Fig. 3.

In conclusion, it was clarified that, for 9-vinylphenanthrenes excepting aromatics having α-substituted vinyl, such as **2e**, the 9,10-double bond, which is only slightly active itself to singlet oxygen, produces, in conjugation with a 9-ethylenic substituent, an active diene system capable of undergoing the 1,4-cycloaddition of singlet oxygen.

Experimental

All melting points are uncorrected. NMR spectra were recorded on a Varian HA-100 spectrometer with TMS as an internal standard. Mass spectra were obtained with a Hitachi RMU-6E spectrometer. The light source consisted of eight 60-W low-pressure sodium vapor lamps (National SOI-60). The yields are based on reacted starting materials.

*Preparation of 9-(2-Methyl-1-propenyl)phenanthrene (**1a**).* To a solution of 9-phenanthrylmagnesium bromide (prepared from 0.023 mol of 9-bromophenanthrene and 0.023 mol of magnesium) in 50 ml of tetrahydrofuran (THF) a THF solution (10 ml) of isobutylaldehyde (0.024 mol) was added at room temperature. After the usual work-up, crude 1-(9-phenanthryl)-2-methyl-1-propanol was dehydrated with phosphorous pentaoxide in hot benzene (80 ml) for 3 h. A benzene solution containing the crude product was washed with a $NaHCO_3$ aqueous solution and dried over $MgSO_4$. The benzene was evaporated and the residual solid was crystallized from ethanol. Thus, **1a** was obtained as colorless granules, mp 66—67 °C, in 57% yield (3.03 g); IR (KBr): 3050, 2920, 1450, 895, 762, 748, 723 cm^{-1}; NMR ($CDCl_3$): δ 1.73 (s, 3H), 2.00 (s, 3H), 6.58 (m, 1H), 7.4—8.7 (m, 9H) ppm; MS *m/e*: 232 (M^+, 41), 217 (48), 116 (31), 108 (93), 101 (100).

*Preparation of 9-Vinylphenanthrene (**1b**).* To a solution of methylenetriphenylphosphorane (prepared from 0.009 mol of methyltriphenylphosphonium bromide and an equimolar amount of butyllithium) in THF (50 ml) was added 9-formylphenanthrene (0.009 mol) at ambient temperature. After 2 h, the reaction mixture was poured into water and extracted with hexane. The hexane solution was dried over $MgSO_4$ and condensed. The residue was chromatographed on silica gel (Wakogel C-200) and eluted with hexane. Thus, **1b** was obtained as a colorless viscous oil in a 60% yield; IR (liquid film): 3070, 1493, 1450, 990, 771, 751, 730 cm^{-1}; NMR (CCl_4): δ 5.47 (d with fine coupling, J=5.5 Hz, 1H), 5.70 (d with fine coupling, J=16 Hz, 1H), 7.2—8.6 (m, 10H).

Preparation of trans-*9-(1-Propenyl)phenanthrene (**1c**).* The olefin, **1c**, was prepared from 9-bromophenanthrene and allyl bromide according to a procedure in the literature.[6)] **1c** was obtained as colorless needles, mp 99—99.5 °C, from hexane (55%) (lit,[6)] bp 157 °C/1.25 Torr); NMR (CCl_4): δ 1.95 (d, J=7.0 and 2.0 Hz, 3H), 6.12 (d of q, J=16.0 and 7.0 Hz, 1H), 6.96 (d with fine couping, J=16.0 Hz, 1H), 7.3—8.6 (m, 9H); MS *m/e* :218 (M^+, 80), 217 (37), 203 (100).

Preparation of trans-*9-Styrylphenanthrene (**1d**).* To a solution of benzylidenetriphenylphosphorane (prepared from 0.0049 mol of benzyltriphenylphosphonium bromide and an equimolar amount of butyllithium) in THF (30 ml) was added 0.0049 mol of 9-formylphenanthrene with stirring for 30 min at room temperature. The reaction mixture was treated as in the case of **1b**. Recrystallization of crude **1d** from ethanol gave colorless granules, mp 118 °C (lit,[6)] 118 °C) (69%); IR (KBr): 3045, 1597, 1495, 960, 746, 740, 692 cm^{-1}; NMR (CCl_4): δ 6.7—8.7 (m, 16H); MS *m/e*: 280 (M^+, 100), 202 (16), 138 (11).

*Preparation of 9-Isopropenylphenanthrene (**1e**).* To a solution of methylenetriphenylphosphorane (prepared from 0.0086 mol of methyltriphenylphosphonium bromide and an equimolar amount of butyllithium) in 50 ml of THF was added 9-acetylphenanthrene (0.0086 mol). Treatment of the crude product similar to the case of **1b** gave colorless crystals, mp 51 °C (lit,[6)] 51 °C) in a 63% yield; IR (KBr): 3060, 1450, 892 cm^{-1}; NMR (CCl_4): δ 2.22 (broad s, 3H), 5.10 (m, 1H), 5.35 (m, 1H), 7.2—8.7 (m, 9H).

*Photooxygenation of 9-(2-Methyl-1-propenyl)phenanthrene (**1a**).* A solution of 0.53 g of **1a** and 5 mg of TPP in 70 ml of CCl_4 was irradiated in an oxygen atmosphere at 5 °C. After 2 h, 53 ml of oxygen was consumed. The photolysate was condensed at room temperature *in vacuo* and the residue was subjected to chromatography on silica gel. Elution with a hexane–CH_2Cl_2 (3 : 1) mixture gave 0.48 g of peroxide **2a** as colorless granules (mp 94—95 °C, from methanol) (80% yield): IR (KBr): 3050, 2975, 1480, 1445, 1060, 1048, 757, 750, 730 cm^{-1}; MS *m/e* :264 (M^+, 24), 246 (49), 232 (59), 221 (41), 205 (42), 202 (42), 178 (93), 176 (49), 165 (68), 43 (100).

Found: C, 81.15; H, 6.08%. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10%.

*Photooxygenation of 9-Vinylphenanthrene (**1b**).* A solution of 1.15 g of **1b** and 5 mg of TPP in 70 ml of CCl_4 was irradiated in an oxygen atmosphere at 5 °C for 5.5 h. The CCl_4 solution was condensed and subjected to chromatography on silica gel. Elution with a hexane–CH_2Cl_2 (3 : 1) mixture gave unreacted **1b** (200 mg) and successively 440 mg of peroxide **2b** (oil): IR (liquid film): 3050, 1450, 1072, 1045, 787, 760, 750 cm^{-1}; MS *m/e*: 237 (M^++1, 33), 205 (100), 179 (47).

Photooxygenation of trans-*9-(1-Propenyl)phenanthrene (**1c**).* Olefin **1c** (0.50 g) and TPP (5 mg) was irradiated in an oxygen atmosphere in 70 ml of CCl_4 for 40 min (O_2 uptake= 54 ml). The CCl_4 was removed from the photolysate under reduced pressure and the residue was purified by chromatography on silica gel in a hexane–CH_2Cl_2 (3 : 1) mixture. Thus, peroxide **2c** (0.54 g) was obtained as colorless granules (from methanol), mp 85—87 °C, in a 94% yield; IR (KBr): 3065, 2975, 1600, 1498, 1450, 1090, 1070, 765, 760, 752, 740 cm^{-1}; MS *m/e*: 250 (M^+, 18), 232 (100), 207 (38), 202 (31), 179 (36), 101 (18).

Found: C, 81.64; H, 5.64%. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64%.

Photooxygenation of trans-*9-Stryylphenanthrene (**1d**).* A solution of 0.95 g of **1d** and TPP (5 mg) in CCl_4 (70 ml) was irradiated for 2 h. After the removal of the CCl_4, the crude product was subjected to chromatography on silica gel and eluted with a hexane–CH_2Cl_2 (3 : 1) mixture. As the first fraction, unreacted **1d** (0.43 g) was recovered and successively peroxide **2d** (0.37 g) was obtained as colorless granules, mp 126—127 °C (from hexane); IR (KBr): 3050, 1450, 1085, 1042, 762, 752, 742, 702 cm^{-1}; MS *m/e*: 312 (M^+, 20), 294 (62), 280 (100), 178 (32).

Found: C, 84.09; H, 5.07%. Calcd for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16%.

*Photooxygenation of 9-Isopropenylphenanthrene (**1e**).* A solution of 0.44 g of **1e** and TPP (5 mg) in CCl_4 (50 ml) was irradiated in an oxygen atomosphere at 5 °C, until the sensitizer faded (6 h, O_2 uptake=21 ml). The photolysate was filtered and condensed *in vacuo* at room temperature. The NMR spectrum (in CCl_4) of the crude photolysate showed the existence of 9-(3-hydroperoxy-1-propen-2-yl)phenanthrene (**6**) [δ 4.70 (m, 2H, $-CH_2OO-$), 5.39 (m, 1H, olefinic) ppm] together with unreacted **1e**. No formation of other compounds, such as endo peroxide **2** and 9-formylphenanthrene, was observed. The chromatographic purification of hydroperoxide **6** on silica gel or alumina was unsuccessful. A KI test (for peroxide) of the crude photolysate was positive.

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