# THE 1,4-CYCLOADDITION OF SINGLET OXYGEN TO 1-VINYLNAPHTHALENES

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Most styrene-type olefins undergo sensitized photooxygenation to give allylic hydroperoxides when they have extractable allylic hydrogens and/or carbonyl compounds as a result of oxidative double-bond cleavage.[1] The only exceptions hitherto known are certain 1,1-diphenyl-2-methoxyethylenes and indenes which have been reported to give products derived from thermally unstable 1,4-cycloadducts of singlet oxygen ($^1O_2$) in the photooxygenation.[2] Whereas some substituted naphthalenes give 1,4-epidioxides in the photo-oxygenation.[3]

The sensitized photooxygenation of 1-vinylnaphthalenes, which formally have all the chromophores active in these type of oxygenation, is the first example of obtaining thermally stable 1,4-cycloadducts of $^1O_2$ from an aromatic-extranuclear unsaturation system.

A solution of 2.00 g of trans-1-styrylnaphthalene (1-a) in 70 ml of $CCl_4$ containing 5 mg of tetraphenylporphine as a sensitizer was irradiated externally with eight 60-W low-pressure sodium vapor lamps (National SOI-60) under an oxygen atmosphere. After 2 hr, an equimolar amount of oxygen was taken up. The reaction mixture was then condensed under reduced pressure, and the residue was chromatographed on silica gel (Wako C-200). Elution with n-hexane-$CH_2Cl_2$ mixture (2:1) afforded a 1,4-endoperoxide 2-a as colorless needles (from a n-hexane-$CH_2Cl_2$ mixture; mp 104.0 - 104.3°) in 55% yield. The NMR spectrum (in $CCl_4$) of 2-a displayed six multiplets centered at $\delta 5.52$ (1H, $H_e$), 5.77 (1H, $H_b$), 6.00 (1H, $H_c$), 6.18 (1H, $H_d$), 6.43 (1H, $H_a$), and 7.28 (9H, aromatic): their coupling constants were as follows; $J_{ab}$= 10.0, $J_{ac}$= 2.8, $J_{bc}$= 2.4, $J_{bd}$= 1.0,

$J_{cd}$= 3.5, $J_{ce}$= 3.5, and $J_{de}$= 4.0 Hz.  Other physical properties·of 2-a were as

follows; ir (KBr) 3025, 2825, 1645, 1630, 1452, 1079, 1070, 1052, 1040, 918, and

860 cm$^{-1}$; uv (EtOH) 293 and 243 nm; m/e 262 (M$^+$, 22), 244 (26), 233 (22), 230

(24), 215 (16), 157 (33), 128 (32), 105 (100), 77 (56), and 51 (21).  Anal.

($C_{18}H_{14}O_2$)C 82.28, H 5.41.  The peroxide 2-a is one of possible two stereo-

isomers in which phenyl and $H_c$ are cis or trans to each other; the structure of

2-a was assigned to the configuration illustrated below based on the stereo-

chemistry 2-d (vide infra).  The formation of peroxides other than 2-a was not

observed in spite of a careful analysis of the crude photolysate.



a: $R^1=C_6H_5$, $R^2=H_e$

b: $R^1$, $R^2$= H

c: $R^1$, $R^2$= $CH_3$

d: $R^1=CH_3$, $R^2$= H

e: $R^1$= H, $R^2$= $CH_3$
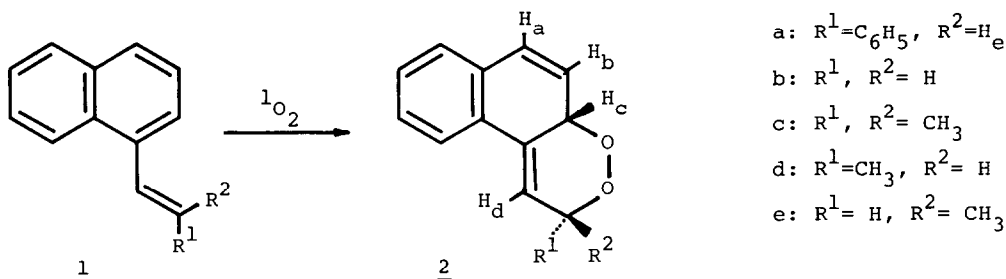
A similar irradiation of 1-vinyl- (1-b) and 1-(2-methylpropenyl)-

naphthalene (1-c) afforded the corresponding 1,4-endoperoxides, 2-b[4] (mp 67 –

68°) and 2-c (oil) in 34 and 78% yields, respectively.  The NMR spectral data

of these peroxides are collected together with those of other endoperoxides in

Table I.

In order to investigate the stereochemistry of the 1,4-cycloaddition of

$^1O_2$ to 1-vinylnaphthalenes, the sensitized photooxygenations of trans-1-

propenylnaphthalene (1-d) and its cis-isomer 1-e[5] were carried out individually.

The olefin 1-d gave a peroxide 2-d as an oil in 55% yield and not its stereo-

isomer 2-e; the latter was obtained as colorless granules (from n-hexane; mp

67 – 68°) from the naphthalene 1-e in 52% yield, though 1-e was less reactive to

$^1O_2$ than the isomer 1-d.  Thus, the 1,4-cycloaddition of $^1O_2$ to 1-vinyl-

naphthalenes was found to proceed stereospecifically.  Furthermore, by comparing

the chemical shifts of the $R^1$ and $R^2$ of the peroxides 2-b~e with each other

(see Table I), we concluded that the peroxide 2-d has an equatorial methyl,

whereas the isomer 2-e has an axial methyl.[6] This means that the suprafacial

attack of $^1O_2$ on 1-vinylnaphthalenes might occur.

Table I.  NMR Spectral Data for 1,4-Endoperoxides (2)

| 1,4-Endo-peroxide | Chemical Shifts in $CCl_4$ ($\delta$ppm) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $H_a$ | $H_b$ | $H_c$ | $H_d$ | $R^1$ | | $R^2$ | |
| | | | | | H | $CH_3$ | H | $CH_3$ |
| 2-b | 6.34 | 5.68 | 5.85 | 5.93 | 5.19 | ---- | 4.44 | ---- |
| 2-c | 6.33 | 5.70 | 5.70 | 5.83 | ---- | 1.51 | ---- | 1.25 |
| 2-d | 6.32 | 5.71 | 5.75 | 5.89 | ---- | 1.51 | 4.55 | ---- |
| 2-e | 6.31 | 5.67 | 5.73 | 5.78 | 5.13 | ---- | ---- | 1.21 |

When 1-isopropenylnaphthalene (1-f) was photooxygenated much as in the

cases described above, no corresponding 1,4-endoperoxide was obtained, but

2-(1-naphthyl)-2-propenyl hydroperoxide (3-f) was obtained in 90% yield; color-

less oil, NMR ($CCl_4$) $\delta4.61$ (s with fine coupling, 2H, $CH_2O$), 5.22 and 5.59

(two m, 2H, olefinic $CH_2$), 7.1 - 8.0 (m, 7H, aromatic), and 8.18 (s, 1H, OOH).

The sensitized photooxygenation of 1-(1-cyclopenten-1-yl)- (1-g) and 1-(1-cyclo-

hexen-1-yl)naphthalene (1-h) also gave the corresponding allylic hydro-

peroxides, 3-g and 3-h, respectively, in yields of more than 90%.  Scarecely

no oxidation of 1-(1-phenylvinyl)naphthalene (1-i) with $^1O_2$ occured.  Thus,

in 1-vinylnaphthalenes, the $\alpha$-substituent on the side chain seemed to inhibit

the 1,4-cycloaddition of $^1O_2$ to the aromatic-extranuclear unsaturation system.
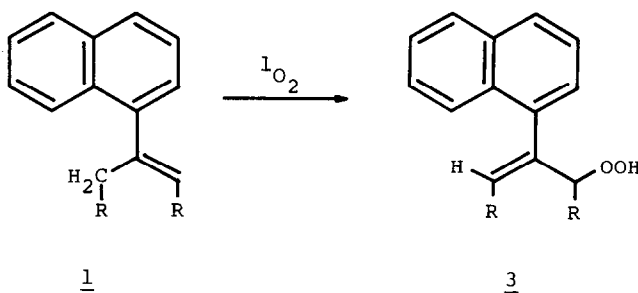


f: R = H

g: R = $-(CH_2)_2-$

h: R = $-(CH_2)_3-$

The sensitized photooxygenation of the other vinyl-substituted polynuclear aromatic hydrocarbons, such as 2-vinylnaphthalenes and 9-vinylphenanthrenes, is now being studied and will be the subject of forthcoming communications.

References and Notes

1. For a review, see R. W. Denny and A. Nickon,"Organic Reactions," Vol. 20, John Wiley & Sons, New York, N. Y., 1973, p 133.

2. C. S. Foote, S. Mazur, P. A. Burns, and D. Lerdal, J. Amer. Chem. Soc., 95, 586 (1973).

3. a) P. -S. Song and T. A. Moore, ibid., 90, 6507 (1968),

   b) J. Rigaudy, Pure Appl. Chem., 16, 169 (1968).

4. All the endoperoxides obtained in this work gave satisfactory analytical data.

5. The olefin 1-e was prepared by the stereospecific hydrogenation of 1-(1-propynyl)naphthalene with a Lindlar catalyst and was purified by fractional distillation (bp 82°/0.3 mm).

6. It is a well-known fact that, in the NMR spectrum, an equatorial proton is consistently found further down field by 0.1 - 0.7 ppm than the axial proton on the same carbon atom in a rigid six-membered ring; a) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison,"Conformational Analysis," John Wiley & Sons, New York, N. Y., 1965, b) R. M. Silverstein and G. C. Bassler,"Spectrometric Identification of Organic Compounds." John Wiley & Sons, New York, N. Y., 1967.  This is also true in the case of a six-membered cyclic peroxide; R. W. Murray, P. R. Story, and M. L. Kaplan, J. Amer. Chem. Soc., 88, 526 (1966).