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ON THE USE OF METHYL SUBSTITUTED POLY(VINYLNAPHTHALENE) AS A REVERSIBLE SINGLET OXYGEN CARRIER[1]

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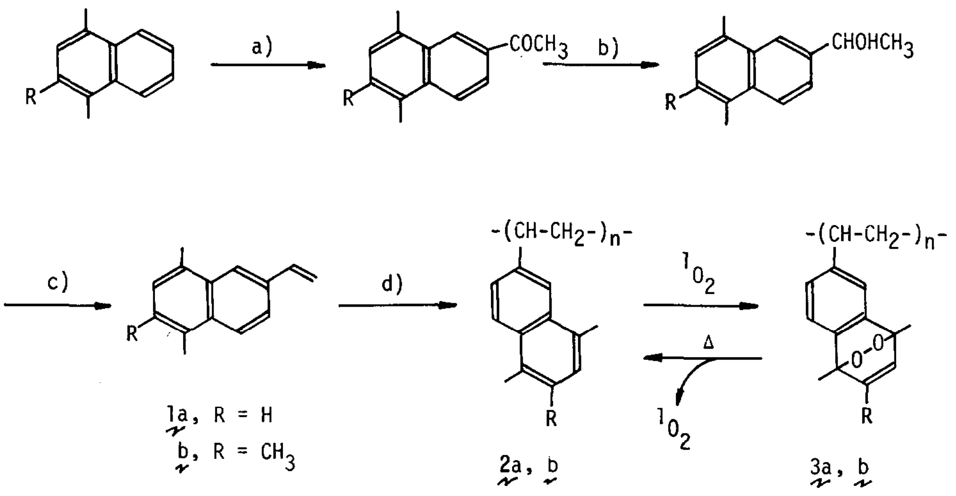
Summary: Poly(1,4-dimethyl-6-vinylnaphthalene) and poly(1,2,4-trimethyl-6-vinylnaphthalene) react with singlet oxygen to give corresponding endoperoxide polymers which on warming generate singlet oxygen efficiently. Singlet oxygenations by the use of these polymers have been described.

Since singlet oxygen was shown to be involved in a variety of chemical and biochemical phenomena, there has been a surge of interest in chemical methods of producing singlet oxygen ($^1O_2$).[2] Development of organic polymers that can absorb and release $^1O_2$ reversibly seems to be particularly useful not only for the purpose of oxygenations of organic substrates but also for the storage of this electronically excited oxygen molecule. We report here that methyl substituted poly(2-vinylnaphthalene) (**2a**,**b**) can absorb $^1O_2$ smoothly at 0 °C to produce corresponding endoperoxide polymers (**3a**,**b**) which on warming to room temperature revert to **2a**,**b** with the liberation of $^1O_2$.[3] The endoperoxide polymers can also be used as a convenient $^1O_2$ source for oxygenations in non-solvent system.[4]

The monomers 1,4-dimethyl-6-vinylnaphthalene (**1a**)[5] and 1,2,4-trimethyl-6-vinylnaphthalene (**1b**)[6] were obtained in straightforward fashion as outlined in Scheme 1.[7] Polymerization of monomers **1a** and **1b** in degassed benzene (AIBN, 70 °C) followed by precipitation from methanol gave **2a** (88%, M.W. 23,000) and **2b** (92%, M.W. 19,000), respectively.

When a solution of polymer **2a** or **2b** in dichloromethane was photooxygenated at 0 °C in the presence of methylene blue, approximately 0.9 equiv mole of oxygen with respect to a naphthalene unit in the polymer was consumed.[9] Removal of the solvent followed by precipitation from methanol gave the corresponding endoperoxide polymers (**3a**,**b**) in almost quantitative yield.

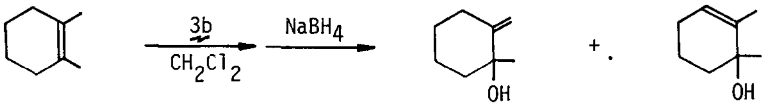
Scheme 1



a) $CH_3COCl/AlCl_3/CH_3NO_2$ b) $LiAlH_4$/ether c) $SOCl_2$, then *t*-BuOK/DMSO

d) AIBN/C_6H_6/70 °C

Warming the solution of 3a in 1,2-dichloroethane to 30 °C gradually produced 2a as evidenced by the appearance of UV absorption of the naphthalene ring, with the concomitant formation of $^1O_2$ (Fig. 1). The kinetic parameters for the thermolysis of the endoperoxide polymers are shown in Table I. The formation of $^1O_2$ was confirmed by the reaction with typical singlet oxygen acceptors such as 1,2-dimethylcyclohexene (4). For example, reaction of 3b (0.45 M eq[10]) and 4 (0.09 M) in dichloromethane (40 °C, 5 h) followed by $NaBH_4$ reduction provided 5 and 6 with the ratio of 94 : 6 (Eq 1).[11] A trapping experiment using 3b (15 mM eq[10]) and 2,5-di-*tert*-butylfuran (30 mM) as a $^1O_2$ trap in dichloromethane at 35 °C under N_2 has shown that $^1O_2$ is liberated in more than 78% yield under the conditions.



(1)

4 5 6

Table I. Kinetic parameters for the thermolysis of endoperoxide polymers (3a,b) in 1,2-dichloroethane[a)]

	Ea (Kcal/mol)	ln A	$\tau_{\frac{1}{2}}$ (min)[b)]
3a	25.8 ± 0.2	34.0 ± 0.3	80
3b	26.9 ± 0.4	34.2 ± 0.1	419

a) Determined by the appearance of naphthalene absorption by UV spectroscopy. b) At 30 °C.

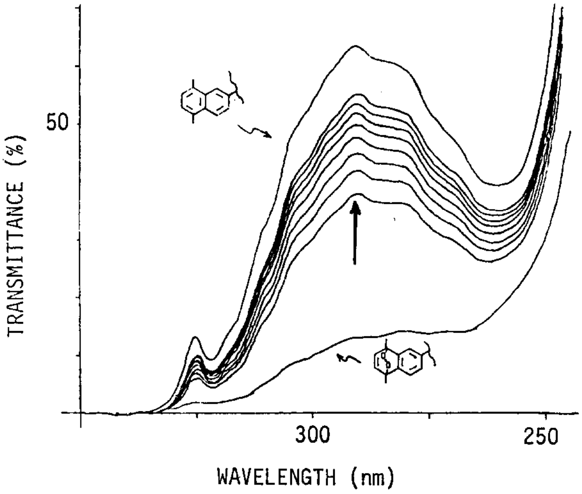
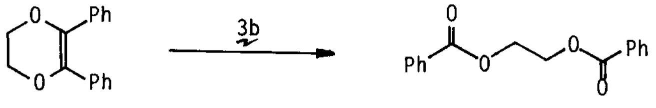


Fig.1

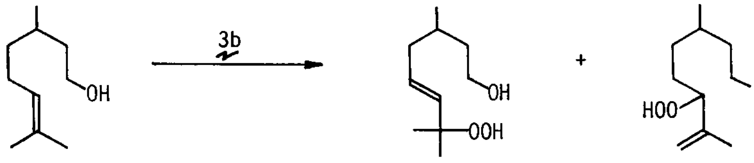
The usefulness of 3b as a $^1O_2$ source is also illustrated by the oxygenations of 2,3-diphenyl-*p*-dioxene (7) and citronellol (8). Warming a solution of 3b (0.2 M eq[10)]) and 7 (0.06 M) in dichloromethane to 40 °C (6 h) produced 9 (96%), whereas heating (40 °C, 6 h) of the film prepared by evaporating the dichloromethane solution of 3b and 7 below 10 °C gave the same product 9 (77%) (Eq 2). Similarly, singlet oxygenation of 8 (0.2 M) by using 3b (1 M eq[10)]) either in solution or film gave a mixture of the hydroperoxides 10 and 11 in almost same ratio as illustrated in Eq 3. After oxygenations resulting polymer 2b was easily recovered by precipitation from methanol and can be reused without further purification.



(2)

7 9

CH_2Cl_2	96%
film	77%



(3)

8 10 11

	10 : 11 = 5 : 4
CH_2Cl_2	50%
film	47%

REFERENCES AND NOTES

1. Photoinduced Reactions 136.
2. R. W. Murray, "Singlet Oxygen", H. H. Wasserman and R. W. Murray, Eds., Academic Press, New York, 1979, p 59.
3. For naphthalene endoperoxides as $^1O_2$ sources, see (a) H. H. Wasserman and D. L. Larsen, J. Chem. Soc. Chem. Commun., 1972, 253; (b) I. Saito and T. Matsuura, ref 2, p 511.
4. For a water-soluble $^1O_2$ source, see I. Saito, T. Matsuura and K. Inoue, J. Am. Chem. Soc., 103, 188 (1981).
5. Mp 48-49 °C; ^1H NMR ($CDCl_3$) δ 2.62 (s, 6 H), 5.31 (dd, 1 H, J = 11, 2 Hz), 5.83 (dd, 1 H, J = 17, 2 Hz), 6.93 (dd, 1 H, J = 17, 11 Hz), 7.13 (bs, 2 H), 7.63 (dd, 1 H, J = 9, 2 Hz), 7.88 (bs, 1 H), 7.96 (d, 1 H, J = 9 Hz).
6. Mp 40-41 °C; ^1H NMR ($CDCl_3$) δ 2.38 (s, 3 H), 2.47 (s, 3 H), 2.56 (s, 3 H), 5.24 (dd, 1 H, J = 11, 2 Hz), 5.78 (dd, 1 H, J = 18, 2 Hz), 6.89 (dd, 1 H, J = 18, 11 Hz), 7.03 (bs, 1 H), 7.51 (dd. 1 H, J = 9, 2 Hz), 7.78 (d, 1 H, J = 2 Hz), 7.89 (d, 1 H, J = 9 Hz).
7. Yields for each step: a) 35% (R = H), 66% (R = Me)[8]; b) 93% (R = H), 82% (R = Me); c) 81% (R = H), 85% (R = Me).
8. The structure of 1,2,4-trimethyl-6-acetylnaphthalene (mp 96.5-97 °C)was confirmed by NOE technique (^1H NMR).
9. The progress of the reaction was monitored by the disappearance of UV absorption of the naphthalene rings.
10. Based on the concentration of a naphthalene endoperoxide unit in the polymer as determined by UV spectroscopy.
11. K. Gollnick and H. J. Kuhn, ref 2, p 287.

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