

THE 1,4-CYCLOADDITION OF SINGLET OXYGEN
TO STILBENES AND β -METHYLSTYRENES

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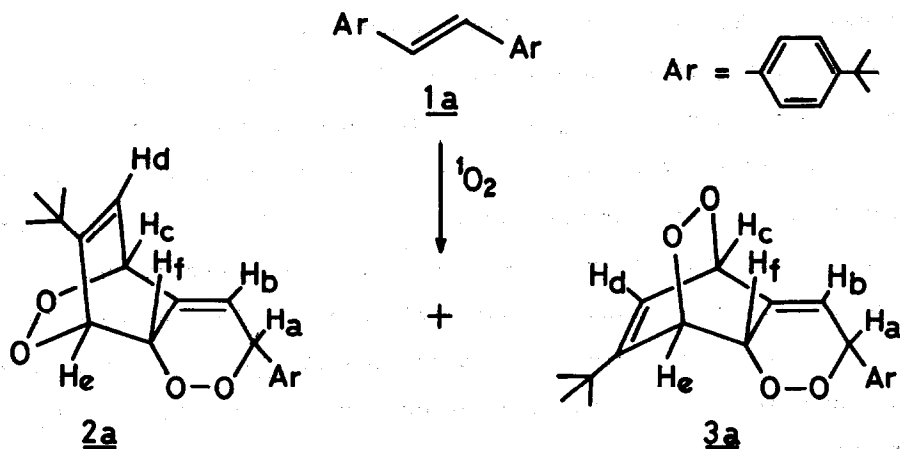
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Sensitized photooxygenation of stilbene¹ and β -methylstyrene² has been reported to induce oxidative double bond cleavage and afford benzaldehyde as the final product. On the other hand, cyclic styrene derivatives, such as indenes³ and dihydronaphthalenes,⁴ and certain 1,1-diphenylethylenes⁵ have recently been found to undergo the 1,4-cycloaddition of singlet oxygen (¹O₂) onto the β -position of the side chain and o-position of the aromatic ring. The above differences of the behaviors between two types of arylethylenes prompted us to reinvestigate the sensitized photooxygenation of stilbenes and β -methylstyrenes including unsubstituted ones in carbon tetrachloride.

The 1,4-cycloaddition of ¹O₂ to the vinyl-substituted aromatics occurred to give the tricyclic peroxides, competing with the other oxygenation modes such as 1,2-dioxetane formation and/or "ene" reaction.

A solution of 1.40 g of trans-4,4'-di-tert-butylstilbene (1a) and 5 mg of tetraphenylporphine in 70 ml of CCl₄ was irradiated externally with eight 60-W low-pressure sodium vapor lamps (National SOI-60) under an oxygen atmosphere until the color of the sensitizer was faded (4 hr, O₂ uptake = 130 ml). After irradiation, the photolysate was condensed under reduced pressure and chromatographed on silica gel (Wako C-200). Elution with benzene gave 682 mg of unreacted 1a, 360 mg (41% yield based on the reacted 1a) of a peroxide 2a (colorless leaflets, mp 122 - 123°C, from ether), and 215 mg (25%) of 3a (colorless granules, mp 127 - 128°C, from a n-hexane - ether mixture), successively. The structures of 2a and 3a were assigned on the basis of their

spectral properties and combustion analyses. The NMR spectrum⁶ (δ in CDCl_3) of 2a displayed two singlets at 1.16 (9H) and 1.29 (9H), and six multiplets centered at 4.57 (1H, H_f), 4.95 (1H, H_c), 4.99 (1H, H_e), 5.31 (1H, H_a), 6.17 (1H, H_b), and 6.28 (1H, H_d) ppm with their coupling constants: $J_{ab} = J_{be} = 2.6$, $J_{bc} = 1.0$, and $J_{cd} = 6.0$ Hz. Whereas, the NMR spectrum (δ in CDCl_3) of 3a showed two singlets at 1.11 (9H) and 1.29 (9H), and six multiplets centered at 4.96 (1H, H_e), 5.05 (1H, H_c), 5.31 (1H, H_f), 5.36 (1H, H_a), 5.67 (1H, H_b), and 6.46 (1H, H_d) ppm with their coupling constants: $J_{ab} = 2.6$, $J_{af} = 1.5$, $J_{cd} = 6.5$, $J_{de} = 2.3$, and $J_{ef} = 3.5$ Hz. The other physical properties of 2a and 3a were as follows; 2a: IR (KBr) 1048, 1038 cm^{-1} ; MS (m/e) 356 (M^+ , 5), 338 (25), 323 (27), 307 (15), 161 (100), 118 (12), 57 (40). Anal. ($\text{C}_{22}\text{H}_{28}\text{O}_4$) C 74.09, H 7.96. 3a: IR (KBr) 1068, 1039 cm^{-1} ; MS (m/e) 356 (M^+ , 2), 324 (11), 322 (13), 307 (15), 295 (31), 161 (100), 118 (12), 57 (55). Anal. ($\text{C}_{22}\text{H}_{28}\text{O}_4$) C 74.57, H 7.57. The structures of 2a and 3a were further confirmed by the use of the NOE technique; in 2a, on irradiation of the tert-butyl signal (at 1.16), a 19% signal increase was observed for H_f proton signal. While in 3a, an NOE was scarcely observed between the tert-butyl group and the H_f proton. In this photooxygenation, 4-tert-butylbenzaldehyde (4a) was scarcely formed.



Similar irradiation of trans-4,4'-dimethylstilbene (1b) gave a mixture of the corresponding peroxides 2b⁷ and 3b together with p-tolualdehyde (4b) (8%). When trans-stilbene (1c) was similarly photooxygenated, the corresponding

endoperoxide 2c was also obtained,⁸ though the major product was benzaldehyde (4c) (80%), which has been reported to be the sole product in previous work.¹ These results are summarized in Table I together with those of β -methylstyrenes. From the facts described above, it is clarified that, in the sensitized photo-oxygenation of stilbenes, the 1,4-cycloaddition of $^1\text{O}_2$ onto the diene system comprised of the ethylenic double bond and an aromatic double bond competes with the 1,2-cycloaddition of $^1\text{O}_2$ onto the ethylenic unsaturation. Furthermore, the addition of $^1\text{O}_2$ by 1,4-mode seems to be the more favorable than that by 1,2-mode, when the more electron-donating substituent is present on the p-position of the aromatic ring of stilbenes.

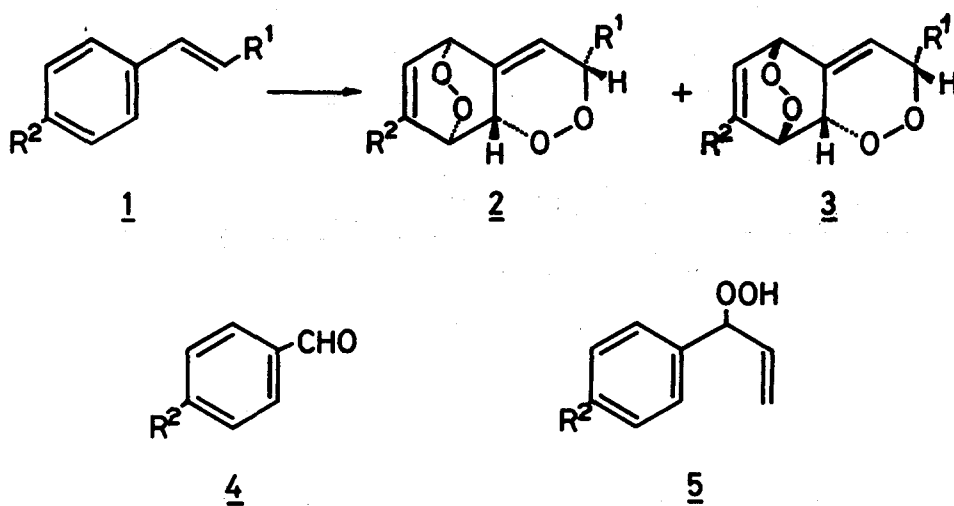
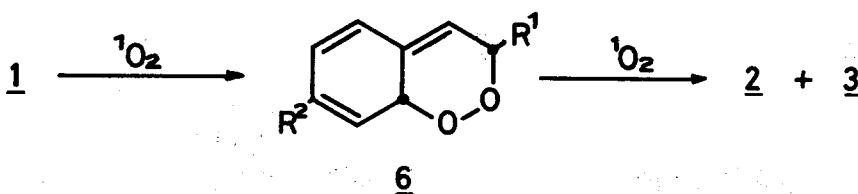


Table I. Endoperoxides of stilbenes and β -methylstyrenes.

<u>1</u>	R^1	R^2	Yield (%)			Mp ($^{\circ}\text{C}$)	
			<u>2</u>	<u>3</u>	<u>2 + 3</u>	<u>2</u>	<u>3</u>
b	p- $\text{CH}_3 \cdot \text{C}_6\text{H}_5$	CH_3	11	10	22	113-4	115
c	C_6H_5	H	16	--	16	103-5	---
d	CH_3	tert- C_4H_9	16	40	56	72-4	110-2
e	CH_3	CH_3	24	16	40	108-10	88-90
f	CH_3	H	13	10	23	91-3	103-5

Similarly, sensitized photooxygenations of 4-tert-butyl- (ld) and 4-methyl-trans- β -methylstyrene (le) were carried out; in both cases, the corresponding stereoisomeric mixtures of the peroxides were obtained as shown in Table I. Unsubstituted trans- β -methylstyrene (lf) was also photooxygenated to give the corresponding endoperoxides 2f and 3f. In these photooxygenations of β -methylstyrenes, the corresponding benzaldehyde 4 (10-15% yield) and a little of the allylic hydroperoxides 5 due to the "ene" reaction (~3%) were also formed. As it is evident from the results in Table I, there was observed a similar tendency of the substituent effects to those of stilbenes in the reactivity of β -methylstyrenes with $^1\text{O}_2$. The peroxides 2 and 3 may be formed through the intermediate 6. This type of the intermediate has been suggested in the sensitized photooxygenation of indenenes, dihydronaphthalenes, and 1,1-diphenylethylenes, in which the type of final products is different from 2 and 3.³⁻⁵



References and Notes

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- (6) TMS was used as internal standard.
- (7) All the endoperoxides 2 and 3 gave satisfactory analytical data.
- (8) Another peroxide 3c could not be obtained.