Chemistry of Singlet Oxygen. XII. Electronic Effects on Rate and Products of the Reaction with Olefins[1]

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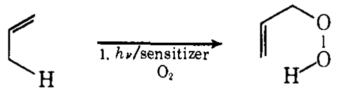
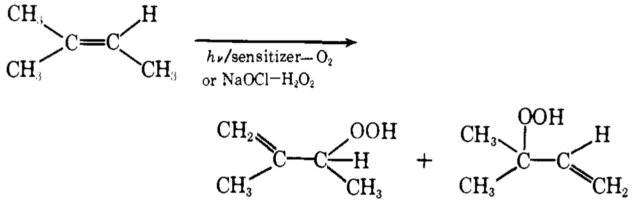
Abstract: Rates and products of photo- and hypochlorite–H_2O_2 oxygenations of ring-substituted α,β,β-trimethylstyrenes (**7**) are determined. The rates of both reactions correlate with σ (ρ = -0.92). The product in each case is a mixture of the 2-methyl-3-phenyl-3-buten-2-ol (**8**) and 3-methyl-2-phenyl-3-buten-2-ol (**9**) in an invariant ratio of about 2.7:1. Epoxidation of the same olefins proceeds with a ρ of -0.87 when the best-fit value of Δr^+ (fraction of σ^+) of 0.37 is used. The singlet oxygen oxygenation is mildly electrophilic, but sensitive mainly to inductive effects, and neither charge nor radical character is localized in the transition state. The product ratio does not appear to be sterically determined.

Recent work has shown that singlet excited molecular oxygen, almost certainly in the $^1\Delta_g$ state, is the reactive intermediate in the dye-sensitized photooxygenations of olefins and polyenes.[2] Comparisons between dye-sensitized oxygenations and reactions of nonphotochemically produced singlet oxygen have shown the intermediates in the two reactions to be identical in stereoselectivity, reactivity, and decay rate.[3] In addition, $^1\Delta_gO_2$ has been detected directly in photosensitized vapor-phase systems by its luminescence[4] and by its characteristic four-line paramagnetic resonance spectrum.[5] In this paper we explore the sensitivity of the reaction to electronic effects and draw some conclusions regarding the transition state for the reaction between singlet oxygen and olefins. In the accompanying paper, these conclusions are combined with the results of solvent effect studies and the mechanism of the reaction is discussed in more detail.[6]

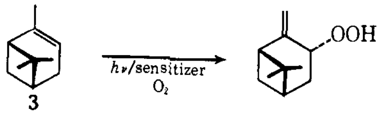
Singlet oxygen adds to olefins which have allylic hydrogens to give allylic hydroperoxides.[2] The double bond shifts cleanly to the allylic position; the course of the reaction is analogous to the Alder "ene reaction."[7]



Previous work has shown that the reaction is quite sensitive to the electron density in the double bond of the olefin. For example, tetraalkyl-substituted olefins are about 20–50 times as reactive as trialkyl-substituted olefins, and these are in turn considerably more reactive than dialkylated olefins.[2,3,8] Electron-withdrawing substitutents such as carbonyl or hydroxyalkyl groups deactivate the olefin.[2] On the other hand, there is very little Markovnikov-type directing effect, with unsymmetrically substituted olefins giving nearly equal amounts of attack at the two ends of the double bond.[2,3] For example, 2-methyl-2-butene produces the two hydroperoxides **1** and **2** in 48 and 52% yield, respectively.[2,3,9] Very similar results are observed with many other cyclic and acyclic olefins. Both the products and the rates of the reactions are very sensitive to steric effects, however. Bulky substituents hinder attack; for example, steroidal olefins are universally attacked principally from the α side and the reaction is often rather slow.[2] α-Pinene (**3**) undergoes substitution almost exclusively on the side away from the gem dimethyl group, and is considerably less reactive than 1-methylcyclohexene.[2,9]



1(48%) **2** (52%)



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The reaction is very sensitive to the conformation of the hydrogen being transferred. For example, 2,4-dimethyl-2-pentene (**4**) gives exclusively hydroperoxide **5**, and none of the other product **6**.[2] The reason for this is believed to be that the conformation required for transfer of the tertiary hydrogen in the transition state leading to **6** is an unfavorable one (conformation a).[2] This olefin is also comparatively unreactive. Similar conformational control of product formation has been observed in steroidal systems.[10]

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[1] Paper XI: C. S. Foote, Y. C. Chang, and R. W. Denny, *J. Amer. Chem. Soc.*, **92**, 5218 (1970); supported by National Science Foundation Grant No. GP-5835 and 8293; taken in part from R. W. Denny, Ph.D. Thesis, University of California, Los Angeles, 1969.

[2] Review: K. Gollnick, *Advan. Photochem.*, **6**, 1 (1968).

[3] C. S. Foote, *Accounts Chem. Res.*, **1**, 104 (1968).

[4] D. R. Snelling, *Chem. Phys. Lett.*, **2**, 346 (1968).

[5] D. R. Kearns, A. U. Khan, C. K. Duncan, and A. H. Maki, *J. Amer. Chem. Soc.*, **91**, 1039 (1969); E. Wasserman, V. J. Kuck, W. M. Delevan, and W. A. Yager, *ibid.*, **91**, 1040 (1969).

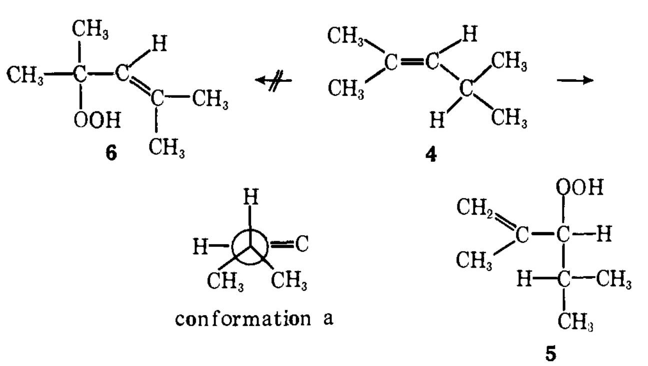
[6] C. S. Foote and R. W. Denny, *J. Amer. Chem. Soc.*, **93**, 5168 (1971).

[7] K. Alder and H. von Brachel, *Justus Liebigs Ann. Chem.*, **651**, 141 (1962), and earlier papers; for a review, see H. M. R. Hoffman, *Angew. Chem., Int. Ed. Engl.*, **8**, 556 (1969).

[8] (a) K. R. Kopecky and H. J. Reich, *Can. J. Chem.*, 43, 2265 (1965); (b) R. Higgins, C. S. Foote, and H. Cheng, *Advan. Chem. Ser.*, No. 77, 102 (1968).

[9] C. S. Foote, S. Wexler, and W. Ando, *Tetrahedron Lett.*, 4111 (1965).

[10] A. Nickon and J. F. Bagli, *J. Amer. Chem. Soc.*, **83**, 1498 (1961); A. Nickon and W. L. Mendelson, *Can. J. Chem.*, **43**, 1419 (1965).

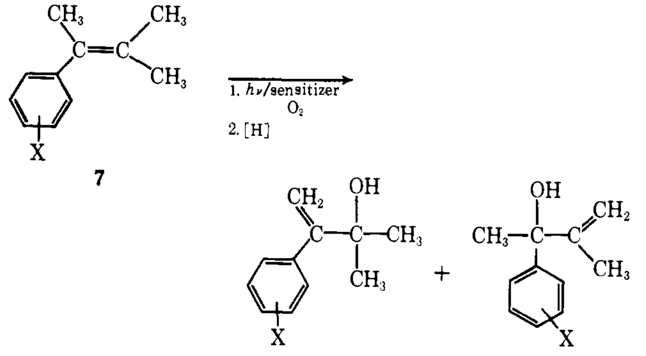

6

4

conformation a

5

Varying steric and conformational effects make evaluation of electronic effects in the preceding examples difficult. The ring substituted α,β,β-trimethylstyrenes (**7**) are compounds with constant steric but variable electronic factors. Photooxygenation of these compounds would be expected to give (after reduction) two products, **8** and **9**; the relative amounts of **8** and **9** as a function of substituent X should yield further valuable information about the transition state for the reaction.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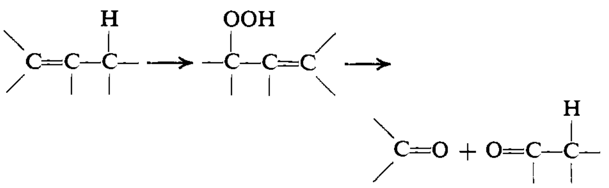
8

9

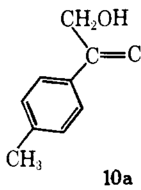
Results

The substituted trimethylstryenes with X = H, *m*- and *p*-$\mathrm{CH_3O}$, *m*- and *p*-Cl, and *m*- and *p*-$\mathrm{CH_3}$ were prepared by addition of the appropriate phenyl Grignard reagent to 3-methyl-2-butanone, followed by dehydration of the resulting alcohol with refluxing 85% $\mathrm{H_3PO_4}$. The resulting trimethylstyrenes contained only a few per cent of the isomeric 3-methyl-2-phenyl-1-butenes, and were further purified by preparative gas chromatography when necessary. The *p*-*N*,*N*-dimethylamino compound was prepared in a similar manner from *p*-*N*,*N*-dimethylaminophenyllithium; dehydration of the alcohol was effected by distillation with a trace of picric acid. The meta and para cyano compounds were made from the meta and para chloro compounds by the Rosenmund–von Braun reaction. The properties of the compounds are in good agreement with expectations, and with the reported properties of those which have been previously prepared.[11]

i. Oxygenation Products. Because photooxygenation of several methylstyrene derivatives was reported to lead exclusively to double bond cleavage (reaction 1), reportedly *via* cleavage of the allylic hydroperoxide,[2,12] precautions were taken to prevent this possible side reaction. The photooxygenations were carried out at 2° in methanol containing 2% pyridine (to avoid any acid catalysts for the cleavage) using Rose Bengal as the sensitizer. Parallel chemical oxygenations were carried out at 2° in methanol-*tert*-butyl alcohol (because of solubility problems with pure methanol) containing $\mathrm{H_2O_2}$ and 2,6-di-*tert*-butylphenol (a radical inhibitor which does not interfere with singlet oxygen reactions[9]) by adding dilute aqueous NaOCl.[13] Oxygenation mixtures were reduced with $\mathrm{NaBH_4}$, and products were isolated by gas chromatography. The products, as expected, were the substituted 2-methyl-3-phenylbuten-2-ols (**8**) and 3-methyl-2-phenyl-3-buten-2-ols (**9**). The spectral and analytical data support the assigned structures unambiguously (see Experimental Section). In the case of the *p*-*N*,*N*-dimethylaminomethylstyrene, it was not possible to isolate the benzylic alcohol product **9**, even at reduced injector temperature. The *p*-$\mathrm{CH_3O}$ compound dehydrates to an extent of 10% under the chromatographic conditions (as shown by reinjection of a pure collected sample). Therefore, since the corresponding saturated alcohol dehydrates so readily on heating, it was assumed that the benzylic product **9** in the *p*-*N*,*N*-dimethylamino case was completely lost under the gas chromatographic conditions, probably by dehydration.


(1)

In order to investigate whether a side reaction such as eq 1 was occurring, *p*-methyltrimethylstyrene was photooxidized at 0 and 42°. At 0°, products **8** and **9** made up 99% of the volatile material. In addition, <1% of 1-*p*-tolylethanol was formed, presumably by reduction of *p*-methylacetophenone produced in a cleavage reaction (the compound was identified by comparison of its retention time with that of an authentic sample). At 42°, the ratio of **8** to **9** had changed significantly; 1-*p*-tolylethanol (2%) and three other compounds, X (10%), Y (6%), and Z (2%), were formed. Although not characterized completely, X, Y, and Z appeared from their ir and nmr spectra to be the three possible primary allylic alcohols **10**, which could have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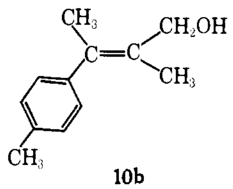
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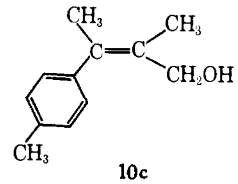
10c

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(11) G. P. Newsoroff and S. Sternhell, *Aust. J. Chem.*, **19**, 1667 (1966).

(12) It has recently been suggested that such cleavages proceed by way of a dioxetane intermediate, instead of the allylic hydroperoxide: W. Fenical, D. R. Kearns, and P. Radlick, *J. Amer. Chem. Soc.*, **91**, 3396 (1969). See also S. Mazur and C. S. Foote, *ibid.*, **92**, 3225 (1970), and P. D. Bartlett and A. P. Schaap, *ibid.*, **92**, 3223 (1970), for related cases.

(13) C. S. Foote, S. Wexler, W. Ando, and R. Higgins, *ibid.*, **90**, 975 (1968).

been formed either by radical autoxidation of the olefin, or by allylic rearrangement of **8** and **9**, a reaction which has been reported for allylic hydroperoxides.[14]

It was concluded that reaction at near 0° was sufficient to prevent any appreciable side reactions. Only trace amounts of compounds corresponding to any of these side products were formed from any of the olefins. The absolute amounts of products were determined by calibrating the detector by injecting solutions of known amounts of pure products and an internal standard (the calibration procedure also corrects for small reproducible losses of products by dehydration; this loss was significant only for **9** in the p-OCH$_3$ and p-N,N-dimethylamino cases). The ratio of the two products formed from each olefin is shown in Table I.

Table I. Product Ratio (**8**/**9**) from Oxygenation of Substituted Trimethylstyrenes[a]

		Ratio	
Substituent	σ^b	Photo-oxygenation[c]	NaOCl–H_2O_2[d]
p-N(CH$_3$)$_2$	−0.83	*e*	*e*
p-CH$_3$O	−0.27	2.80[f]	2.91[f]
p-CH$_3$	−0.17	2.70	2.63
m-CH$_3$	−0.07	2.71	2.52
H	0.00	2.48	2.47
m-CH$_3$O	+0.12	2.44	2.48
p-Cl	+0.23	2.71	2.65
m-Cl	+0.37	2.63	2.68
m-CN	+0.56	2.84	2.79
p-CN	+0.66	2.86	2.92

[a] After reduction with NaBH$_4$; corrected for detector response factors; average of at least three runs in each case; average standard deviation is ±0.16 in the ratio. [b] From E. Kosower, "An Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1968. [c] Rose Bengal sensitized, in CH$_3$OH–2% pyridine. [d] With 10^{-2} M 2,6-di-*tert*-butylphenol in 50% CH$_3$OH-*tert*-butyl alcohol. [e] Not measurable because of loss of **9**. [f] Roughly 10% loss of **9** has been corrected for.

ii. **Reaction Rates.** Relative reaction rates were determined by the competition technique described by Higgins, Foote, and Cheng.[8b] The kinetic treatment is based on that of Ingold and Shaw,[15] as derived for this system.[8b] Solutions containing weighed mixtures of the two olefins were oxidized as described above. After reduction, the amount of each product formed was determined by gas chromatography, using an internal standard, added after the reaction. The relative reactivities are listed in Table II.

The value of β for p-chlorotrimethylstyrene (the ratio of the decay rate for singlet oxygen to its reaction rate[2,3,8b]) was calculated from the β value for 2-methyl-2-butene, 0.12 M,[16] and the rate for p-chlorotrimethylstyrene relative to 2-methyl-2-butene (Rose Bengal sensitized, in methanol, determined by the competition technique to be 2.23). The β value for p-chlorotrimethylstyrene thus determined is 0.054 M.

Table II. Relative Rates of Oxygenation of Substituted Trimethylstyrenes

	Rel rate[a]	
Substituent	Photooxygenation[b]	NaOCl–H_2O_2[c]
p-N(CH$_3$)$_2$[d]	3.90	5.00
p-OCH$_3$	1.96	1.27
p-CH$_3$	1.42	1.26
m-CH$_3$	1.00	0.95
H	(1.00)	(1.00)
m-OCH$_3$	0.945	0.909
p-Cl	0.649	0.664
m-Cl	0.545	0.550
m-CN	0.280	0.315
p-CN	0.245	0.194

[a] Calculated from the average of at least three analyses in each case. [b] Rose Bengal sensitized, in CH$_3$OH–2% pyridine. [c] In 50% *tert*-butyl alcohol–methanol containing roughly 0.01 M 2,6-di-*tert*-butylphenol. [d] Rates calculated assuming the unobserved product **9** was actually formed in ratio **8**/**9** = 2.70.

The data are plotted against the Hammett σ in Figures 1 and 2. The value of ρ for the photooxygenation is -0.93 ± 0.06, and that for OCl–H$_2$O$_2$ oxygenation is -0.91 ± 0.07. The correlation coefficients were 0.987 and 0.980, respectively. The correlation is significantly lowered by plotting against the Brown σ^+ parameter. An attempt to improve the fit using the Yukawa–Tsuno equation[17] which defines a composite parameter by blending σ and σ^+ showed that the optimum fit was obtained when less than 10% of σ^+ was added. Considering the low precision of the data caused by the small rate spread, use of the more complex treatment is not justified.

iii. **Epoxidation Studies.** Because it is probable that the double bond in the trimethylstyrenes is not coplanar with the ring because of steric interference,[18] it was desirable to evaluate the amount by which resonance inhibition affected the photooxygenation rates. For this reason, the relative rates of epoxidation with perbenzoic acid in benzene were measured by the competition technique[15] for some of the olefins. The product epoxides were separated by gas chromatography, and their spectral and analytical data were in accord with expectations. The results are summarized in Table III.

Table III. Relative Epoxidation Rates of Substituted Trimethylstyrenes with Perbenzoic Acid in Benzene at 29.5°

Substituent	Rel rate
p-OCH$_3$	2.16
H	1.00
m-OCH$_3$	0.89
p-Cl	0.76
m-Cl	0.48

The epoxidation rates correlate rather poorly with either σ or σ^+, and a significantly better correlation was achieved by use of the Yukawa–Tsuno treatment;[17] the plot is shown in Figure 3. The optimum value of r (the fraction of σ^+ in the blended parameter) was 0.37 and the corresponding ρ was -0.87.

iv. **2,3,4-Trimethyl-2-pentene.** In order to assist in the evaluation of possible steric effects on the oxygenation products, 2,3,4-trimethyl-2-pentene (**11**) was

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(14) G. O. Schenck, O. A. Neumüller, and W. Eisfeld, *Justus Liebigs Ann. Chem.*, **618**, 202 (1958); B. Lythgoe and S. Trippet, *J. Chem. Soc.*, 471 (1959); W. F. Brill, *J. Amer. Chem. Soc.*, **90**, 975 (1968).

(15) C. K. Ingold and F. R. Shaw, *J. Chem. Soc.*, 2918 (1927).

(16) Gollnick reports a value of 0.055 M.[2] The value used above was obtained from the previously determined[8b] rate for 2-methyl-2-butene relative to 2-methyl-2-pentene, 1.26, and the measured value of β in methanol for 2-methyl-2-pentene, 0.15 M.[6] Because of the pyramiding of errors, the absolute β values for p-chlorotrimethylstyrene may be in error by as much as a factor of 1.5.

(17) Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Jap.*, **32**, 965 (1959).

(18) H. Suzuki, *ibid.*, **33**, 613 (1960).

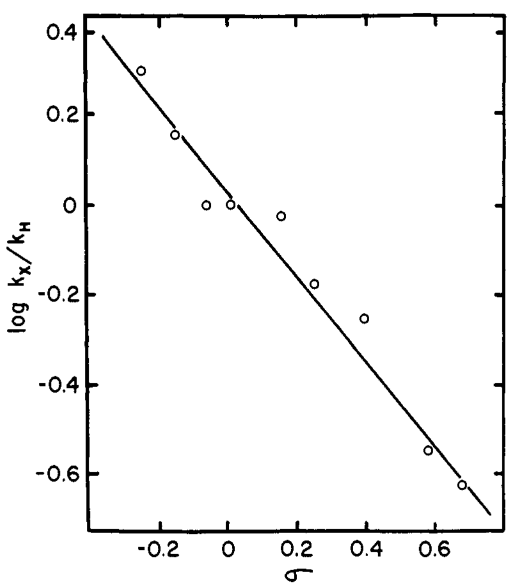


Figure 1. Hammett plot for Rose Bengal sensitized photooxygenation of substituted 2-methyl-3-phenyl-2-butenes in CH_3OH–2% pyridine.

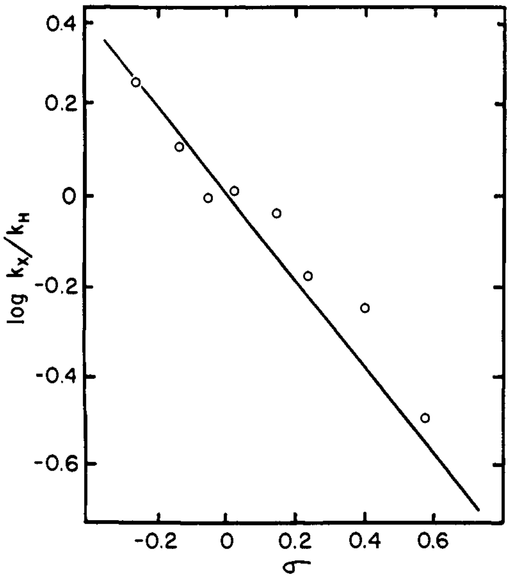
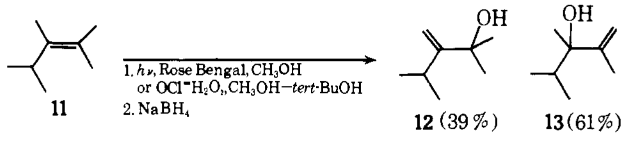


Figure 2. Hammett plot for OCl^-–H_2O_2 oxygenation of substituted 2-methyl-3-phenyl-2-butenes in CH_3OH-*tert*-BuOH, 1:1.

prepared and oxygenated under the same conditions used for the styrenes. Both photosensitized and OCl^-–H_2O_2 oxygenation gave, after reduction, a mixture of two allylic alcohols **12** and **13** in a ratio of 2:3. The products were characterized by their spectral and analytical data.



In accord with previous results with isopropyl-substituted olefins,[2] none of product **14** (which would require abstraction of the isopropyl hydrogen) was formed, presumably because of the unfavorable conformation of this hydrogen for transfer, as mentioned previously.

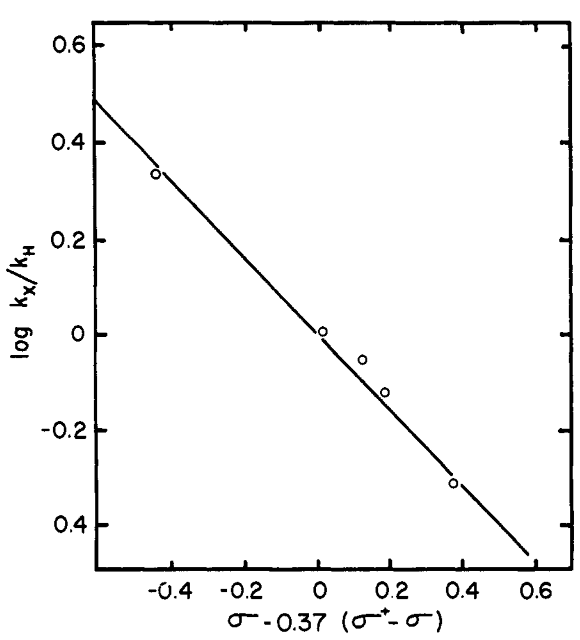
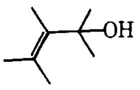


Figure 3. Yukawa–Tsuno plot of epoxidation rates of substituted 2-methyl-3-phenyl-2-butenes with perbenzoic acid in benzene, 29.5°, $r = 0.37$.



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Discussion

As with all previous cases,[3] the results of the photooxygenations and of the OCl^-–H_2O_2 oxygenations are identical within experimental error, as would be expected if the reactive intermediate in both reactions is singlet oxygen.

The oxygenation reactions are mildly electrophilic ($\rho = -0.92$). This electrophilicity is consistent with the rate-increasing effect of methyl groups previously noted,[2,3,8] and is comparable with that of the reaction with perbenzoic acid. The correlation with σ indicates that no great resonance electron demand is made on the substituents at the transition state; this behavior contrasts with that with perbenzoic acid, where the best fit is obtained with a parameter containing 37% σ^+. The value of ρ required to fit the epoxidation data for the trimethylstyrenes (-0.87) is close to that reported for ring-substituted styrenes (-1.3),[19] and a comparable fraction of σ^+ is necessary (0.37 and 0.48, respectively); the differences are in the direction of slightly less electron demand for the trimethylstyrenes than for the styrenes, as might have been expected. The data therefore indicate that lack of coplanarity of the trimethylstyrene double bond with the aromatic ring does not represent a serious barrier to the transmission of electron density by resonance in the epoxidation reaction, and therefore, presumably also not in the photooxidation. The electron demand of the singlet oxygen oxygenations therefore appears not to involve extensive resonance.

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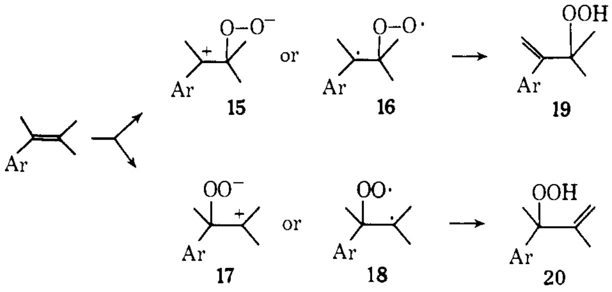
(19) Y. Ishii and Y. Inamoto, *J. Chem. Soc. Jap., Ind. Chem. Sect.*, **63**, 765 (1960).

The product distribution in the oxygenations is almost totally independent of the substituent on the aromatic ring. Examination of the results of a very large number of determinations shows that the ratio of nonbenzylic alcohol **8** to benzylic alcohol **9** may be slightly lower for the unsubstituted trimethylstyrene ($X = H$) than for the others, but as the differences are no larger than the combined standard deviations, it seems unwise to draw any conclusions from this fact. The lack of variation is consistent with the absence of a Markovnikov-type directing effect previously noted in unsymmetrically substituted olefins,[2,3,9] and suggests that the product-determining transition state possesses neither localized charge nor localized radical character. The lack of exalted resonance effects on the rate is also consistent with the lack of charge localization. If ionic or radical structures **15–18** contributed appreciably to the structure of the transition state, electron-donating substituents should stabilize **15** relative to **17**; either electron-withdrawing or electron-donating substituents which could resonate with a free radical should stabilize **16** relative to **18**, and the result should be that product **19** would be favored relative to **20**.



The results reported here suggest that the electron density in the double bond as a whole influences the reaction rate, but that the effect is not localized on one of the atoms.

The reason for the predominance of isomer **19** over the benzylic isomer **20** is difficult to state with certainty. It does not appear that the steric effect of the phenyl group forces the oxygen to attack predominantly at the less hindered carbon, at least to the extent that the isopropyl group in 2,3,4-trimethyl-2-pentene (**11**) is a steric model for the phenyl group, since the preponderance of product **13** in the oxygenation of this olefin is in precisely the opposite direction. The bearing of the rate and product data on various possible reaction mechanisms is discussed in the accompanying paper.[6]

Experimental Section

Ir spectra were taken in CCl_4, unless otherwise stated; nmr spectra were recorded at 60 MHz in CCl_4–2% TMS; uv spectra were recorded in hexane. Mass spectra were taken on an AEI MS-9 by Sharon Jones, and are reported as per cent of the base peak. Microanalyses were by H. King. The vpc retention times are expressed relative to 2,6-di-*tert*-butylphenol as standard (1.0) on 10% Carbowax 20 M.

2-Methyl-3-phenyl-2-butene. To a solution of C_6H_5MgBr in ether (from 78.5 g (0.5 mol) of C_6H_5Br) was added 34.5 g (0.4 mol) of 3-methyl-2-butanone in ether. The solution was refluxed 2 hr, and quenched with ice, followed by dilute HCl. The mixture was extracted with ether, and the extracts were washed with saturated $NaHSO_3$ solution, 10% $NaHCO_3$, and water. Phosphoric acid (10 ml of 85%) was added to the residue after ether removal, and the solution refluxed for 2 hr at 170°. The aqueous layer was removed, and the product distilled, bp 187–193°. The product contained 6% of the isomeric 2-phenyl-3-methyl-1-butene, and was purified by vpc on an 8-ft column of 10% Bentone 34 on 60–80 Chromosorb W at 130°. The yield was 14 g (43%). The nmr and uv spectra agree with reported values.[11]

Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.34; H, 9.69. Except for those cases detailed below, other starting olefins were prepared in a similar manner and had satisfactory spectra and analyses.

2-Methyl-3-*N*,*N*-dimethylaminophenyl-2-butene. A solution of 38 g (0.6 mol) of *n*-butyllithium in 500 ml of hexane was added under N_2 to a solution of 100 g (0.5 mol) of *p*-bromo-*N*,*N*-dimethylaniline in 300 ml of dry ether. After stirring at room temperature for 1.5 hr, 90 g (1.05 mol) of 3-methyl-2-butanone in 300 ml of dry ether was added and the solution was refluxed 1 hr. After addition of 200 ml of H_2O, an 18% HCl solution was added until the solution was acidic, and then a concentrated NaOH solution was added until the pH was above 10. The ether–hexane layer was removed and dried over anhydrous $MgSO_4$.

After evaporation of the ether–hexane solvent and addition of 0.1 g of picric acid, fractional distillation yielded 75 g (40%) of 2-methyl-3-*p*-*N*,*N*-dimethylaminophenyl-2-butene: bp 90–95° (0.14 mm). The spectra were analogous to those of the other olefins.

2-Methyl-3-*p*-cyanophenyl-2-butene. A solution of 10 g (0.055 mol) of 2-methyl-3-(*p*-chlorophenyl)-2-butene, 10 g (0.11 mol) of CuCN, and 75 ml of quinoline was heated under reflux for 24 hr at 230° under N_2. After cooling, 200 ml of a 20% NH_4OH solution and 300 ml of ether were added, the NH_4OH layer was removed, and the ether layer was extracted twice with NH_4OH solution. The ether layer was washed once with water, three times with 8 *N* HCl and then 5% $NaHCO_3$, and then with saturated NaCl. The solution was dried over anhydrous $MgSO_4$ and the ether removed. Fractional distillation yielded 2.7 g (30%) of 2-methyl-3-*p*-cyanophenyl-2-butene; bp 70–76° (0.09 mm). The spectra were analogous to those of the other olefins. The *m*-cyanophenyl compound was prepared in the same way.

Sensitized Photooxygenation of 2-Methyl-3-phenyl-2-butene. A solution of 0.3 g (3×10^{-4} mol) of Rose Bengal, 0.8 g (5.5 mol) of 2-methyl-3-phenyl-2-butene, and 2 ml of pyridine in 97 ml of methanol was irradiated in an ice bath cooled immersion apparatus through which oxygen was recirculated. The light source was a 625-W Sylvania Sungun incandescent lamp, regulated at 75 V by a Sola constant voltage transformer. The light was first filtered through 0.5 cm of a 0.2 *M* $CuSO_4$ solution before entering the reaction vessel.

After 12 min of irradiation, 99 ml (4.4 m mol, 80%) of O_2 was taken up. A solution of 0.4 g (0.10 mmol) of $NaBH_4$ in 40 ml of methanol was added with stirring. An aliquot was removed for determination of the product distribution. The residue after solvent evaporation was dissolved in ether, washed four times with water, and filtered through charcoal and anhydrous $MgSO_4$. The solution was condensed and injected at 160° into a 7 ft × $^3/_8$ in. column containing 10% Carbowax 20M on 80–100 Chromosorb W. The major product, 2-methyl-3-phenyl-3-buten-2-ol (**8**), was collected after 12 min (relative retention time 0.99). The nmr spectrum had peaks at τ 2.78 (m, 5), 4.54 (d, 1, J = 1.8 Hz), 5.07 (d, 1, J = 1.8 Hz), 6.50 (1), and 8.63 (6). The uv spectrum had only a shoulder at 220 mμ (log ϵ 3.7) in addition to the weak benzene ring absorption. The ir spectrum had prominent peaks at 2.78, 2.90, 3.28, 3.36, 6.12, 6.72, 7.26, 7.34, 7.61, 8.50, 8.60, 8.98, 9.20, 9.70, 10.47, 10.90, 11.26, and 14.31 μ. The mass spectrum had the parent peak at 162 (0.25%), the base peak at 129, and prominent peaks at 128 (60%) and 144 (42%).

The minor product, 2-phenyl-3-methyl-3-buten-2-ol (9), was collected after 15 min (*rt* = 1.4). The nmr spectrum had peaks at τ 2.75 (m, 5), 4.90 (m, 1), 5.16 (m, 1), 7.25 (1), and 8.45 (6). The ir spectrum had prominent peaks at 2.77, 2.84, 3.30, 3.40, 6.70, 6.91, 7.32, 7.61, 8.36, 9.44, 9.73, 11.06, and 14.33 μ. The uv spectrum had a slight shoulder at 210 mμ (log ϵ 4.0). The mass spectrum had the parent peak at 162 (0.05%), the base peak at 129, and prominent peaks at 128 (55%) and 144 (40%). Other photooxygenations were run similarly; the products had analogous spectra and properties.

Oxygenation of 2-Methyl-3-phenyl-2-butene with $NaOCl$–H_2O_2. A solution containing 0.8 g (5.5 mmol) of 2-methyl-3-phenyl-2-butene, 0.1 g (4.8×10^{-4} mol) of 2,6-di-*tert*-butylphenol, 0.6 g (20 mmol) of H_2O_2 (2.3 ml of a 30% aqueous solution), 50 ml of methanol, and 50 ml of *tert*-butyl alcohol was stirred vigorously in a flask immersed in an ice bath. After the internal temperature of the solution was below 2°, 0.6 g (8 mmol) of NaOCl (4 ml of a 14% aqueous solution) was added dropwise without allowing the temperature to rise above 5°. The solution was reduced with 0.9 g (24 mmol) of $NaBH_4$, an aliquot was removed for measurement of the isomer distribution, and the remaining solution was worked up as described previously (no charcoal used). Conversion to products was intentionally incomplete.

Relative Rates of Photooxygenation of 2-Methyl-3-(*p*-tolyl)-2-butene and 2-Methyl-3-*p*-cyanophenyl-2-butene. A solution containing 0.4464 g (2.79 mmol) of 2-methyl-3-(*p*-tolyl)-2-butene, 0.4791 g (2.80 mmol) of 2-methyl-3-(*p*-cyanophenyl)-2-butene, 0.3 g (3×10^{-4} mol) of Rose Bengal, 2 ml of pyridine, and 97 ml of methanol was irradiated as previously described. After 3.5 min, 58 ml of O_2 was taken up (45% completion). A solution containing 0.4 g (0.01 mol) of $NaBH_4$ in 40 ml of methanol was added. After 30 min, a solution containing 0.1619 g (1.17×10^{-3} mol) of β-phenoxyethanol as internal standard in 30 ml of methanol was added. The solution was injected onto a 6 ft × 1/8 in. Carbowax 20M column on 80–100 Chromosorb W and the relative peak areas were obtained from the average of three chromatograms. Detector response factors were determined by injecting solutions containing weighed samples of the four allylic alcohol products, obtained by preparative vpc from previous photooxidations, and β-phenoxyethanol. Photooxygenations for other olefin pairs were carried out similarly.

Relative Rates of Reaction of 2-Methyl-3-(*p*-tolyl)-2-butene and 2-Methyl-3-(*p*-cyanophenyl)-2-butene with $NaOCl–H_2O_2$. A solution containing 0.351 g (2.05 mmol) of 2-methyl-3-(*p*-cyanophenyl)-2-butene, 0.303 g (1.89 mmol) of 2-methyl-3-(*p*-tolyl)-2-butene, 0.15 g of 2,6-di-*tert*-butylphenol, 2.3 ml of a 30% H_2O_2 solution (20 mmol), 50 ml of *tert*-butyl alcohol, and 50 ml of methanol was stirred vigorously in a flask immersed in an ice bath. When the temperature of the solution became less than 2°, 4 ml of 14% NaOCl solution (80 mmol) was added dropwise at a speed which did not raise the temperature of the solution above 5°. After completion of the NaOCl addition, 0.9 g (0.01 mol) of $NaBH_4$ in 30 ml of methanol was added. After 30 min, 0.0851 g (6.16×10^{-4} mol) of β-phenoxyethanol in 30 ml of methanol was added. The actual amounts of the allylic alcohol products formed were determined from their vpc peak areas, corrected for detector response and product decomposition, relative to the vpc peak area of β-phenoxyethanol, as described previously. The results of oxygenations of various olefin pairs are summarized in Table IV.

Table IV. Relative Rates of Reaction (k_A/k_B) of Olefin Pairs (A and **B**) and Isomer Distributions (**8**/**9**) in Oxygenations of the Various 2-Methyl-3-phenyl-2-butenes

Olefin A/B	Photo k_A/k_B	**8A/9A** **8B/9B**	$H_2O_2–OCl^-$ k_A/k_B	**8A/9A** **8B/9B**
p-CH_3/*p*-CH_3O	1.00/1.38	2.70 2.80	1.00/1.33	2.63 2.91
H/*p*-CH_3O	1.00/1.96	2.48	1.00/1.75	2.47
p-Cl/*p*-CH_3	0.457/1.00	2.71	0.526/1.00	2.65
m-Cl/*p*-CH_3	0.384/1.00	2.63	0.436/1.00	2.68
m-CH_3/*p*-Cl	1.54/1.00	2.71	1.433/1.00	2.52
p-CN/*p*-CH_3	0.172/1.00	2.86	0.154/1.00	2.92
m-CN/*p*-CH_3	0.197/1.00	2.84	0.252/1.00	2.79
p-CH_3/H			1.20/1.00	
m-CH_3O/*p*-CH_3	0.667/1.00	2.44	0.721/1.00	2.48
p-$(CH_3)_2N$/*p*-CH_3O	2.0/1.00	(2.80)/ 2.80	2.9/1.00	(2.91)/ 2.91

Relative Reactivity of Various 2-Methyl-3-phenyl-2-butenes with Perbenzoic Acid in Benzene. A solution containing 0.2578 g (1.43 mmol) of 2-methyl-3-(*m*-chlorophenyl)-2-butene, 0.3027 g (2.09 mmol) of 2-methyl-3-phenyl-2-butene, and 100 ml of benzene was stirred vigorously in a thermostated water bath at 29.5° and 20 ml of a 0.02 *M* solution of perbenzoic acid in benzene was added dropwise. The resulting solution was stirred for 2 hr, 0.1744 g (1.13 mmol) of *o*-nitroanisole was added as internal standard, and the resulting solution was analyzed on a 1/8 in. × 6 ft 10% Carbowax 20M column previously injected with ethylenediamine. (At 130° on a column previously injected with benzoic acid and without ethylenediamine, 90% of the 2-methyl-3-(*p*-anisyl)-2,3-epoxybutane was lost, forming mainly 2-methyl-3-(*p*-anisyl)-3-buten-2-ol). Detector response values for the products were determined as previously.

The nmr spectrum of 2-methyl-3-phenyl-2,3-epoxybutane had peaks at τ 2.74 (5), 8.45 (3), 8.60 (3), and 9.10 (3). The ir spectrum had prominent peaks at 3.28, 3.42, 6.21, 6.70, 6.85, 6.91, 7.29, 7.90, 8.20, 8.79, 8.98, 9.32, 9.54, 9.76, 10.96, 11.48, 12.01, and 14.3 μ. The mass spectrum had the parent peak at 162 (2.8%) and the base peak at 78. The retention time was 0.24. Other epoxides had similar properties.

2,3,4-Trimethyl-2-pentene. A solution of 170 g (1 mol) of 2-iodopropane in 140 ml of ether was added dropwise to 120 ml of ether containing 24.3 g (1 g-atom) of magnesium. After refluxing for 45 min, a solution containing 86 g (1 mol) of 3-methyl-2-butanone in 140 ml of ether was added dropwise and the solution refluxed for 3 hr. After addition of 100 ml of H_2O and 200 ml of an 18% HCl solution, the aqueous layer was removed and the ether solution was washed with a $NaHSO_3$ solution. The ether was removed on the rotary evaporator, 8 ml of 85% H_3PO_4 was added, and the olefin was distilled from the reaction mixture. Since several isomeric olefins were present, the olefin was purified on a preparative column containing 10% Carbowax-20 on 80–100 Chromosorb W.

The nmr spectrum of 2,3,4-trimethyl-2-pentene had peaks at τ 7.16 (m, probably heptuplet with outer peaks covered by baseline noise, 1, *J* = 7 Hz), 8.38 (6), 8.49 (3), and 9.09 (d, 6, *J* = 7 Hz). The ir spectrum had prominent peaks at 3.31, 3.41, 6.10 (very weak), 6.85, 7.30, 7.39, 8.66, 9.00, 9.10, and 9.51 μ. The mass spectrum had the parent peak at 112 (31%), the base peak at 55, and prominent peaks at 97 (87%) and 41 (36%).

2-Methyl-3-(2′-propyl)-3-buten-2-ol. The nmr spectrum of 2-methyl-3-(2′-propyl)-3-buten-2-ol had peaks at τ 4.99 (m, 1), 5.26 (d, 1), 7.71 (m, 2), 8.71 (6), and 8.95 (d, 6, *J* = 7 Hz). The ir spectrum had prominent peaks at 2.70, 3.30, 6.05, 6.88, 7.21, 7.30, 7.71, 8.60, 8.71, 9.09, 9.31, 9.71, 10.05, 10.72, and 11.10 μ. The mass spectrum had the parent peak at 128 (0.02%), the base peak at 43, and prominent peaks at 113 (22%), 85 (52%), 59 (59%), and 41 (35%).

2,3,4-Trimethyl-1-penten-3-ol. The nmr spectrum of 2,3,4-trimethyl-1-penten-3-ol had peaks at 5.12 (1), 5.27 (1), 8.27 (5), 8.81 (3), and 9.17 (doublet, 6, *J* = 7 Hz). The ir spectrum had prominent peaks at 2.71, 3.31, 6.08, 6.84, 7.26, 7.35, 7.62, 8.48, 8.63, 9.01, 10.42, 10.51, 10.81, 11.09, 11.36, and 14.34 μ. The mass spectrum had the parent peak at 128 (1.7%), the base peak at 85, and prominent peaks at 57 (47%), 43 (62%), and 41 (41%).

2,3,4-Trimethyl-3-penten-2-ol. Although 2,3,4-trimethyl-3-penten-2-ol was not observed, a small amount (≤5%) could have escaped detection under the 2,3,4-trimethyl-1-penten-3-ol peak on the vpc.

Photooxygenation of 2-Methyl-3-(*p*-tolyl)-2-butene at 42°. A solution of 0.8 g (5.5 mmol) of 2-methyl-3-(*p*-tolyl)-2-butene, 0.5 g (5×10^{-4} mol) of Rose Bengal, 2 ml of pyridine, and 97 ml of methanol was irradiated at 42° and worked up as described previously. Analysis of the reaction mixture by vpc indicated a yield of 17% 2-methyl-3-(*p*-tolyl)-3-buten-2-ol (**9**), 63% 2-(*p*-tolyl)-3-methyl-3-buten-2-ol (**7**), 2% 1-(*p*-tolyl)ethanol (identified by comparison of the retention time of a known sample), 10% compound X, 6% compound Y, and 2% compound Z.

Compound X was tentatively identified as 2-(*p*-tolyl)-3-methyl-2-buten-1-ol by the nmr spectrum, which had peaks at τ 3.04 (4), 5.90 (2), 6.86 (1), 7.73 (3), 8.21 (3), and 8.45 (3). Compound Y was identified as 2-methyl-2-(*p*-tolyl)-*cis*-buten-1-ol by the nmr spectrum, which had peaks at τ 3.04 (4), 6.22 (2), 7.25 (1), 7.71 (3), 8.09 (3), and 8.20 (3). Compound Z was tentatively identified as 2-methyl-3-(*p*-tolyl)-*trans*-2-buten-1-ol by the nmr spectrum, which had peaks at τ 3.04 (4), 5.86 (2), 7.00 (1), 7.70 (3), 8.09 (3), and 8.31.