room temperature, $DDQH_2$ (2.5 g) precipitated from the dark brown reaction mixture. Vacuum evaporation of solvent from the filtrate left a brown crystalline residue which was recrystallized by dissolving in methylene chloride and adding hexane to yield 1.45 g (64%) of tan colored crystals: mp 160–161 °C; NMR ($CDCl_3$) δ 2.33 (br s, 3 H, CH_3), 3.08 (s, 3 H, SO_2CH_3), 7.90 (m, 1 H), 8.07 (d, J = 2.5 Hz, 1 H), 9.93 (s, 1 H, CHO), 11.73 (s, 1 H, OH). Anal. Calcd for $C_9H_{10}O_4S$ (mol wt, 214.24): C, 50.46; H, 4.70. Found: C, 50.41; H, 4.62.

3,5-Di-*tert*-butyl-2-hydroxydiphenylcarbinol (7d). A solution of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (2.34 g, 10 mmol) in ether (50 mL) was treated with phenyllithium solution (2 molar equiv). Vacuum evaporation of solvent after addition of methanol left a residue which was dissolved in aqueous acetic acid. Extraction of the aqueous solution with petroleum ether (bp 40–60 °C) gave an oily product which crystallized when treated with pentane to yield 2.2 g (70%), mp 95–97 °C. Anal. Calcd for $C_{21}H_{28}O_2$ (mol wt, 312.46): C, 80.73; H, 9.03. Found: C, 80.77; H, 9.07.

3,5-Di-*tert*-butyl-2-hydroxybenzophenone (8d) was recrystallized from aqueous ethanol to give yellow crystals, mp 60–62 °C. Anal. Calcd for $C_{21}H_{26}O_2$ (mol wt, 310.44): C, 81.25; H, 8.44. Found: C, 81.30; H, 8.40.

Oxidation of 4,6-Di-*tert*-butyl-2-(hydroxymethyl)phenol by DDQ in Methanol (20). DDQ (9.08 g, 40 mmol) was added to a solution of **5c** (9.44 g, 40 mmol) in methanol (55 mL). After about 15 min a pale yellow crystalline material started to precipitate. Filtration after 72 h gave 9.38 g (54%) of pale yellow crystalline product, mp 234–236 °C. Recrystallization by dissolving in acetone and adding methanol did not raise the melting point. Anal. Calcd for $C_{22}H_{22}Cl_2N_2O_3$ (mol wt, 433.34): C, 60.98; H, 5.12. Found: C, 61.25; H, 5.10.

Vacuum evaporation of solvent from the filtrate obtained after isolation of **20** gave a solid residue which was treated with methylene chloride. Filtration gave 3.4 g (37%) of $DDQH_2$. The solid residue obtained from the filtrate after vacuum evaporation of solvent was subjected to vacuum sublimation (5×10^{-2} torr, bath temperature 60 °C). The yield of sublimed 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde was 3.3 g (35%); mp 58–60 °C.

Diacetate 21. A solution of **20** (1 g) in 2 M acetic anhydride in ethyl acetate/perchloric acid (20 mL) was kept at room temperature for 2 h and then diluted with methanol (20 mL). Vacuum evaporation of solvents gave a crystalline colorless residue which was recrystallized from boiling aqueous methanol to yield 820 mg: mp 168–169 °C; NMR ($CDCl_3$) δ 1.25 (s, 9 H, *t*-Bu), 1.38 (s, 9 H, *t*-Bu), 2.27 (s, 3 H, Ac), 2.48 (s, 3 H, Ac), 6.57 (d, J = 2.5 Hz, 1 H), 7.27 (d, J = 2.5 Hz, 1 H). Anal. Calcd for $C_{26}H_{26}Cl_2N_2O_5$ (mol wt, 517.41): C, 60.36; H, 5.07. Found: C, 60.55; H, 5.07.

Diacetate 22. Acetylation of **20** (2 g) with acetic anhydride (20 mL) in the presence of pyridine (0.5 mL) at room temperature (24 h) gave an isomeric diacetate (1.5 g): mp 138–141 °C; NMR ($CDCl_3$) δ 1.32 (s, 9 H, *t*-Bu), 1.45 (s, 9 H, *t*-Bu), 1.85 (s, 3 H, Ac), 2.45 (s, 3 H, Ac), 6.98 (d, J = 2.5 Hz, 1 H), 7.33 (d, J = 2.5 Hz, 1 H). Anal. Calcd for $C_{26}H_{26}Cl_2N_2O_5$ (mol wt, 517.41): C, 60.36; H, 5.07. Found: C, 60.56; H, 5.08.

Acknowledgment. We are indebted to the Chemical Products Division of Crown Zellerbach, Camas, WA, for a gift of 2-hydroxymethyl-6-methyl-4-(methylthio)phenol.

Registry No. 1a, 100-51-6; **1b**, 589-18-4; **1c**, 7705-64-8; **1d**, 620-24-6; **1e**, 4383-06-6; **1f**, 623-05-2; **1g**, 498-00-0; **1h**, 530-56-3; **1i**, 22002-17-1; **1j**, 88-26-6; **2a** DNP, 1157-84-2; **2b** DNP, 2571-00-8; **2c**, 66-39-7; **2d**, 100-83-4; **2e**, 621-59-0; **2f**, 123-08-0; **2g**, 121-33-5; **2h**, 7311-34-4; **2i**, 2314-36-5; **2j**, 1620-98-0; **3a**, 73049-07-7; **3b**, 73049-08-8; **3c**, 19566-78-0; **3d**, 19566-76-8; **3e**, 19566-77-9; **3f**, 19566-75-7; **3g**, 73049-09-9; **3h**, 73049-10-2; **3i**, 73049-11-3; **3j**, 10061-52-6; **3k**, 20017-35-0; **4a**, 2491-32-9; **4b**, 66476-02-6; **4c**, 73049-12-4; **4d**, 73049-13-5; **4e**, 73049-14-6; **4f**, 14035-39-3; **4g**, 73048-86-9; **4h**, 73048-87-0; **4i**, 5384-09-8; **4j**, 5650-43-1; **4k**, 14035-34-8; **5a**, 90-01-7; **5b**, 13464-23-8; **5c**, 16373-02-7; **5d**, 10496-92-1; **5e**, 73048-88-1; **6a** DNP, 1160-76-5; **6b**, 1666-01-9; **6c**, 37942-07-7; **6d**, 1666-03-1; **6e**, 73048-89-2; **7a**, 91-01-0; **7b**, 833-39-6; **7c**, 20017-39-4; **7d**, 40473-49-2; **8a**, 119-61-9; **8b**, 1137-42-4; **8c**, 7175-89-5; **8d**, 24242-58-8; **9a**, 2085-90-7; **9b**, 15982-67-9; **10a**, 495-71-6; **10b**, 13145-56-7; **11a**, 955-83-9; **11b**, 57196-75-5; **19**, 530-55-2; **20**, 73048-90-5; **21**, 73048-91-6; **22**, 73048-92-7; DDQ, 84-58-2; benzyl chloride, 100-44-7; 3,5-diphenyl-4-hydroxybenzaldehyde, 3437-80-7; 2-(hydroxymethyl)-6-methyl-4-(methylthio)phenol, 32867-65-5.

Structure and Reactivity of α,β-Unsaturated Ethers. 17. Oxidations by Permanganate and Osmium Tetraoxide

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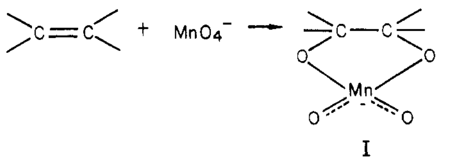
Rates of the reactions of various enol ethers with potassium permanganate and osmium tetraoxide in aqueous solution and carbon tetrachloride, respectively, have been measured at 30 °C. The reactions of some alkenes and acrylates were also examined for the sake of comparison. The osmium reaction was found to be electrophilic, while the permanganate reaction was accelerated by both electron-donating and -attracting groups. β-Alkyl substitution enhanced the reactivity of vinyl ether while an α-methyl group exerted little effect in both reactions. The trans isomers were found to be more reactive than the cis counterparts. The results can be rationalized by assuming a transition state resembling intermediate cyclic esters.



(1)

I

Permanganate and osmium tetraoxide are well-known as useful oxidants which convert an olefin to a cis diol.[1,2] The primary step of these oxidations has been established to be the formation of cyclic ester, I or II.[1-5] The cyclic osmate II was actually isolated,[4] and the manganate I has recently been detected spectrophotometrically.[5] The rates

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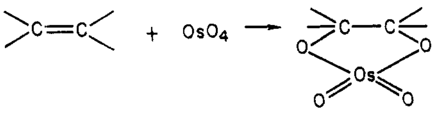


(2)

II

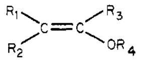
of the formation of I were measured with various olefinic carboxylic acids,[6-10] alcohols,[6,11] and some other olefins.[12,13] The osmium tetraoxide oxidation of 3-cyclohexenecarboxylic acid has been kinetically investigated.[14] Substituent effects on the oxidation rates of stilbene were examined by competitive experiments.[13] All the kinetic results can be interpreted in terms of the formation of the cyclic ester intermediates; the resemblance of the kinetic behavior with that of the 1,3-dipolar cycloaddition has been noted.[6] On the other hand, Sharpless et al.[15] have recently suggested the intermediacy of an organometallic osmium compound in the course of the formation of the cyclic ester II. Thus, the transition state of the reactions has not been well characterized.

Comparisons of the kinetic results of these reactions with those of other addition reactions appear to be of value for deepening our understanding of the nature of the oxidation process. For such investigations, enol ethers may be most suitable as substrates. Extensive studies have already been conducted on their electrophilic additions[16-18] as well as cycloadditions.[19,20] In this report we describe our kinetic results on the oxidations of various enol ethers in comparison with the previous results on sulfenylation. The electronically symmetric nature of the transition state of both reactions was deduced. Furthermore, the reactions of some other olefins, including acrylates, were examined, the results showing an interesting contrast in polar effects of substituents between the two reactions.

Experimental Section

Materials. Potassium permanganate (Yoneyama Chemicals) and osmium tetraoxide (Wako Pure Chemicals) were of analytical grade and used without further purification. Pyridine (KOH), tetrahydrofuran (CaH_2), and carbon tetrachloride (P_2O_5) were refluxed over drying agents and distilled. All the ethers were obtained as described previously.[16] Other olefins commercially available were distilled. Isomeric purity was >98% by GLC.

Table I. Rate Constants for the Oxidations of Alkenyl Alkyl Ethers



no.	R_1	R_2	R_3	R_4	$10^{-3}k_2$, $M^{-1}\ s^{-1}$ ($KMnO_4$)	k_2, $M^{-1}\ s^{-1}$ (OsO_4)
1	H	H	H	CH_3	0.608	0.172
2	H	H	H	C_2H_5	0.825	0.434
3	H	H	H	i-C_3H_7	1.02	0.821
4	H	H	H	t-C_4H_9	0.648	0.965
5	H	H	H	n-C_4H_9	0.781[a]	0.417[b]
6	H	H	H	i-C_4H_9	0.555	0.410
7c	H	CH_3	H	C_2H_5	5.06	6.17
7t	CH_3	H	H	C_2H_5	17.3	10.2
8c	H	CH_3	H	i-C_3H_7	3.62	5.98
8t	CH_3	H	H	i-C_3H_7	18.5	24.0
9c	H	C_2H_5	H	CH_3	4.95	4.74
9t	C_2H_5	H	H	CH_3	9.40	4.03
10c	H	C_2H_5	H	C_2H_5	3.72	5.60
10t	C_2H_5	H	H	C_2H_5	11.3	8.66
11c	H	C_2H_5	H	i-C_3H_7	2.15	7.13
11t	C_2H_5	H	H	i-C_3H_7	9.76	15.5
12	CH_3	CH_3	H	C_2H_5	15.6	38.9
13	H	H	CH_3	C_2H_5	0.291	0.566

[a] $\Delta H^{\ddagger} = 4.4 \pm 1.1$ kcal/mol, $\Delta S^{\ddagger} = -31 \pm 4$ eu. [b] $\Delta H^{\ddagger} = 8.6 \pm 0.3$ kcal/mol, $\Delta S^{\ddagger} = -32 \pm 1$ eu.

Permanganate Reaction. Rates were measured by means of a stopped-flow spectrophotometer, Union RA-1100. A stock solution of the olefin, except for acrylates, was prepared by mixing an appropriate amount of olefin (usually about 5×10^{-5} mol), 1 mL of THF, and 3 mL of 1 M aqueous NaOH in a 25-mL mess flask and adding glass-distilled water to fill the flask at room temperature. In the same way, potassium permanganate was dissolved in glass-distilled water (1×10^{-4} M). Stock solutions of an olefin and the oxidant were thermally equilibrated at 30.0 ± 0.1 °C in separate reservoirs of the stopped-flow apparatus and then mixed by the pressure drive. The decrease in absorbance at 530 nm (MnO_4^-) was recorded by means of a high-speed memory unit (Union RA-108S) and displayed on a recorder (National VP-6421A). In the reaction of acrylates, alkali was added to the permanganate solution instead of the acrylate solution to avoid the ester hydrolysis. Although permanganate(VII) changed gradually to manganate(VI) in alkaline solution,[3] some small contamination of the latter in the reaction mixture did not affect the overall kinetics of the reaction.

Osmium Tetraoxide Reaction. Stock solutions of an olefin (usually about 5×10^{-3} M) and OsO_4 ($\sim 2 \times 10^{-2}$ M) in CCl_4 were prepared by weighing. The olefin solution contained a small amount (usually 1.0×10^{-3} M) of pyridine. Three milliliters of the olefin stock solution was thermally equilibrated at 30.0 ± 0.1 °C in a stoppered quartz cuvette inserted in a water-jacketed cell holder. Into the olefin solution was added 30 μL of the oxidant solution with the use of a microsyringe. The reaction was monitored by the increase in absorbance at 307 nm with a Shimadzu UV-200 spectrophotometer. The pseudo-first-order plots were linear over 80% of the reaction.

Results

Kinetic measurements in the reactions of various olefins were carried out by following spectrophotometrically the disappearance of an oxidant (MnO_4^-) or the formation of an oxidant (OsO_4)–olefin adduct. Thus, the reaction rates measured correspond to the rates of the formation of 1:1 oxidant–olefin adducts (cyclic esters).[2-5] All the runs were carried out in the presence of a large excess of an olefin, obeying the pseudo-first-order kinetics.

Permanganate Reaction. The reaction was carried out in an alkaline aqueous solution ([NaOH] = 0.06 M). A

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Table II. Rates of the Reactions of Olefins with $KMnO_4$ and OsO_4

no.	olefin	$10^{-2}k_2$, $M^{-1}\ s^{-1}$ ($KMnO_4$)	$10^{2}k_2$, $M^{-1}\ s^{-1}$ (OsO_4)
2	$CH_2{=}CHOC_2H_5$	8.25	43.4
14	$CH_2{=}CHC_6H_5$	9.68	6.63
15	$CH_2{=}CHC_4H_9$	0.282	6.09
16c	$CH_3CH{=}CHC_4H_9$ (cis)	0.551	19.6
16t	(trans)	0.637	27.5
17	$CH_2{=}CHCO_2CH_3$	25.8	1.29
18t	$CH_3CH{=}CHCO_2CH_3$ (trans)	10.5	0.619
19	$CH_2{=}C(CH_3)CO_2CH_3$	26.0	1.93

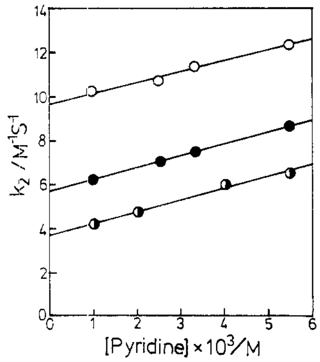

Figure 1. Dependence of the second-order rate constants, k_2, on the pyridine concentration in the reaction of osmium tetraoxide with 5 (◑), 7c (●), and 7t (○). The rate constants for 5 are multiplied by 10.

small amount of tetrahydrofuran (2 vol %) was used as a cosolvent to solubilize the olefins. The aqueous THF solution decolorized permanganate only very slowly (k = 0.03 s^{-1} at 30.0 °C). The rates of olefin oxidation were much greater in most cases, but some slow reactions needed corrections by blank experiments. The pseudo-first-order rate constants were proportional to the olefin concentration in the range [olefin] = (1.0–5.0) × 10^{-3} M. That is, the rates were first order in each reactant (eq 3).

$$\begin{aligned} \text{rate} &= k_1[MnO_4^-] \\ &= k_2[MnO_4^-][\text{olefin}] \end{aligned} \qquad (3)$$

The second-order rate constants k_2 obtained for enol ethers are summarized in Table I. β-Alkyl substitution enhanced the reactivity of vinyl ethers, and all the trans isomers were several times more reactive than the cis counterparts. The results for the other olefins are given in Table II. Both electron-donating and -attracting substituents seem to enhance the reactivity of ethylene.

Osmium Tetraoxide Reaction. The reaction was conducted in CCl_4 in the presence of a small amount of pyridine.[14] The effect of pyridine concentration on the observed pseudo-first-order rate constants k_1 was examined, and results are shown in Figure 1 for 5 and 7. In the concentration range of (1.0–5.5) × 10^{-3} M, the k_1 values change linearly with [pyridine] (eq 4). The second-order

$$k_1 = k_0 + k_{py}[\text{pyridine}] \qquad (4)$$

term in pyridine observed previously[14] was not found under the present conditions (low pyridine concentration). The pseudo-first-order rate constants obtained with constant pyridine concentrations were exactly proportional to the olefin concentration in the range (5.7–16) × 10^{-3} M (eq 5).

$$\begin{aligned} \text{rate} &= k_1[OsO_4] \\ &= k_2[OsO_4][\text{olefin}] \end{aligned} \qquad (5)$$

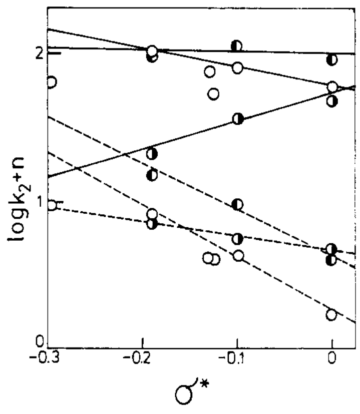

Figure 2. Correlations of the rate constants k_2 with Taft's σ^* values of alkyl groups for permanganate (solid lines) and osmium tetraoxide oxidations (dashed lines) of alkyl vinyl (○), *cis*-1-butenyl (◑), and *trans*-1-butenyl ethers (◐).

The k_2 values obtained at [pyridine] = 1.0 × 10^{-3} M are given in Tables I and II. Reactivity of monosubstituted ethylenes decreases in the order $(CH_3)_3CO > (CH_3)_2CHO > C_2H_5O > CH_3O > C_6H_5 \approx C_4H_9 > CH_3CO_2$. Methyl and ethyl substitutions for vinylic hydrogen enhance the reactivity of vinyl ethers. The trans isomers are more reactive than the corresponding cis isomers with one exception (9).

Discussion

Effects of the Alkoxy Groups. Data given in Table I show that rates of the osmium reaction of the ethers increase in the order $CH_3O < C_2H_5O < (CH_3)_2CHO < (CH_3)_3CO$, while those of the permanganate reaction vary only slightly in an irregular order as is obvious in the plots of log k_2 vs. Taft's σ^* values (Figure 2). The regression lines have been drawn through the points for the methyl, ethyl, and isopropyl ethers.

In Figure 2, the slopes (ρ^*) of all three lines for the osmium reaction are negative, which may reflect the electrophilic nature of the reaction in accord with the previous results.[13] Downward deviations of the points for the *tert*-butyl, isobutyl, and *n*-butyl vinyl ethers suggest the occurrence of adverse steric effects. Such steric effects are reflected also in the magnitudes of slopes for different substrate groups. The absolute magnitudes of slopes decrease in the order vinyl (−3.6) > *trans*-1-butenyl (−3.1) > *cis*-1-butenyl ethers (−0.93). Steric requirements for the reaction must increase in this order.

The results for the permanganate reaction are more illuminating. The slopes (ρ^*) range from negative to positive; the slope for vinyl ethers is negative (−1.2), that for *trans*-1-butenyl ethers nearly zero, and that for *cis*-1-butenyl ethers positive (1.9). These observations are also reconciled with the concept of the dual (i.e., electronic and steric) effects of alkyl substituents. Thus, the reaction of the ethers would innately be weakly electrophilic but greatly liable to suffer steric effects. In the case of *cis*-1-butenyl ethers, the steric effects must be so large that the apparent slope can well be positive. The positive slope need not be taken as an indication of the nucleophilic nature of the reaction.

Effects of Polar Substituents. The electrophilic nature of the osmium reaction found with enol ethers seems to extend to olefins in general. The data in Table II indicate that the reactivities of monosubstituted ethylenes decrease with the electron-attracting character of the substituents ($C_2H_5O > C_6H_5 > C_4H_9 > CH_3CO_2$). In accord with these results, the reaction of substituted stilbenes was characterized with the Hammett ρ value of −0.55.[13]

Table III. Effects of Alkyl Substitution on the Reactivity of Ethyl Vinyl Ether (2) in the Oxidation and Related Reactions

		rel reactivity		
no.	substituent	$KMnO_4$	OsO_4	C_6H_5SCl[a]
13	α-CH_3	0.35	1.3	1.1
7[b]	β-CH_3	14	19	15
12	β,β-$(CH_3)_2$	19	90	17
10[b]	β-C_2H_5	10	17	50

[a] Taken from ref 18. [b] Averages of cis and trans derivatives.

By contrast, both electron-donating (RO) and electron-withdrawing substituents (CH_3CO_2) accelerate the permanganate reaction of ethylene. This reaction was previously considered to be nucleophilic from the results with substituted stilbenes ($\rho = +0.65$),[13] while it seems to be weakly electrophilic from the above results with enol ethers. This apparent contradiction might be reconciled by the concept of orbital-controlled reaction.

In terms of the charge-transfer interaction between olefin and oxidant at the transition state, osmium tetraoxide is an acceptor and the olefin a donor. That is, the interaction between the LUMO of OsO_4 and the HOMO of the olefin is important, and electron-rich olefins are more reactive. In the case of the permanganate reaction, both the LUMO and HOMO of MnO_4^- might be important for the interaction with olefin. Thus, the electron-rich olefin behaves as a donor while the electron-deficient olefin behaves as an acceptor. The apparent polar nature of the reaction is consequently complicated and may be nucleophilic,[13] electronically insensitive,[6,7] or even electrophilic, depending on the nature of olefins.

Effects of Alkyl Substitution. The effects of α- and β-alkyl substitutions on the reactivity of ethyl vinyl ether are summarized in Table III. The data show clearly that the β-alkyl substitution enhances the rates of both reactions while an α-methyl substitution affects them only slightly. The accelerating effects of the β-alkyl groups seem to be greater in the osmium reaction than in the permanganate reaction. The second methyl group of the β,β-dimethyl derivative **12** further enhances the reactivity of **7** in the OsO_4 reaction, while it exerts little influence on the MnO_4^- reaction. In the latter reaction the adverse steric effects may have counterbalanced the rate-enhancing electronic effects of the methyl group. The steric effects in the former reaction may be relatively small as compared with the electronic effects.

The tendency pointed out above resembles that observed previously in the sulfenyl chloride addition,[18] as is seen in the last column of Table III. A similar tendency of reactivities seems to occur also in the ozonation of alkenes although the change is small.[21] Furthermore, resemblance between the permanganate oxidation and the 1,3-dipolar addition was pointed out by Wiberg.[6] All these results are consistent with a transition state of an electronically symmetric structure. The results of secondary isotope effects support this consideration.[7] A transition-state structure resembling the intermediate cyclic ester, I or II, would be most reasonable for the present oxidation processes.

Relative Cis/Trans Reactivity. Table IV summarizes the relative reactivities of geometric isomers of alkenyl ethers. The values less than unity indicate greater reactivity of trans isomers. In most cases, trans isomers are more reactive than the corresponding cis isomers. The results are in contrast with those observed in electrophilic additions of positively charged species, where cis olefins are generally more reactive than the trans isomers.[16-18,22]

Table IV. Relative Cis/Trans Reactivities of Alkenyl Alkyl Ethers, RCH=CHOR′, in the Oxidation Reactions

				cis/trans reactivity	
no.	R	R′	$H°$,[a] kcal/mol	$KMnO_4$	OsO_4
7	CH_3	C_2H_5	0.37	0.29	0.60
8	CH_3	i-C_3H_7	−0.57	0.20	0.25
9	C_2H_5	CH_3	(1.1)	0.53	1.2
10	C_2H_5	C_2H_5	0.27	0.33	0.65
11	C_2H_5	i-C_3H_7	(−0.5)	0.22	0.46

[a] Enthalpy change on going from trans to cis isomers.[27] Values in parentheses are estimated.

The greater reactivity of cis isomers toward cationic species was ascribed to the coulombic term of the interaction energies at the transition state.[16b,23] It is also suggested that the charge-transfer interaction is of dominant importance in homolytic reactions of olefins,[23] where trans isomers are led to exhibit greater reactivity as compared to cis isomers.[24-26] The present results as listed in Table IV could be rationalized in terms of charge transfer; *the charge-transfer interaction at the transition state* should favor trans isomers to show greater reactivity. The cis/trans reactivity of a given ether is uniformly greater in the osmium reaction than in the permanganate reaction. This may reflect the stronger electrophilic nature of the former reaction. In the exceptional case of **9**, the cis isomer is more reactive for some additional reason.

Inspection of the magnitudes of relative cis/trans reactivities shows that they decrease in the order **9** > **10** > **7** > **11** > **8** for both reactions. This order is identical with the decreasing order of $\Delta H°$, the enthalpy change on going from the trans to cis isomers.[27] That is, the relative reactivity of the trans isomers tends to decrease as their relative ground-state stability increases. Thus, the cis/trans reactivities observed here appear to be somehow related to the relative ground-state stability as well. The greater reactivity of *cis*-**9** as compared to *trans*-**9** in the osmium reaction can be accounted for from this last reasoning.

Further Comments on the Transition State Structure. As has been suggested above, the transition states of the present reactions structurally resemble the intermediate cyclic esters I and II. Recently, Sharpless et al.[15] have claimed that organometallic intermediates are involved in the oxidations of olefins by osmium tetraoxide as well as chromyl chloride. They suggest that the formation of π and/or σ complexes should precede the formation of the intermediate II in the osmium reaction. If so, the transition state would resemble the π or σ metal complex since the cyclic intermediate should be relatively

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(21) D. G. Williamson and R. J. Cvetanovic (*J. Am. Chem. Soc.* **1968**, *90*, 3668, 4248) reported, e.g., the relative reactivity of propene to isobutene to *cis*-2-butene to be 1:1.2:2.

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stable. However, the Pd^{II}-catalyzed oxidation of olefins, which has been established to proceed via such a metal complexation, reveals a structure–reactivity relationship quite different from the one observed here. Methyl substitutions, for instance, reduce the reactivity of alkenes.[28] Likewise, the stabilities of Ag$^+$–olefin complexes are reduced by the alkyl substitutions.[29,30] In addition, cis isomers usually form more stable Ag$^+$ complexes.[29,30]

Sharpless questioned why the electron-rich oxygen terminus of OsO_4 should attack an olefin electrophilically.[15] As noted above, the electrophilic nature of the osmium reaction is not very strong, and the charge-transfer interaction is important at the transition state. In other words, the reaction must be orbital-overlap controlled rather than net-charge controlled. The effect of net-charge density, if any, would be of secondary importance, and the reaction could well be electrophilic because of the presence of a low-lying vacant orbital (LUMO) in OsO_4.[31] The transition state like II is reasonable also from the orbital-symmetry considerations.[32]

Registry No. 1, 107-25-5; 2, 109-92-2; 3, 926-65-8; 4, 926-02-3; 5, 111-34-2; 6, 109-53-3; 7c, 4696-25-7; 7t, 4696-26-8; 8c, 4188-64-1; 8t, 4188-65-2; 9c, 10034-12-5; 9t, 10034-13-6; 10c, 4884-01-9; 10t, 1528-20-7; 11c, 16969-28-1; 11t, 16969-13-4; 12, 927-61-7; 13, 926-66-9; 14, 100-42-5; 15, 592-41-6; 16c, 6443-92-1; 16t, 14686-13-6; 17, 96-33-3; 18t, 623-43-8; 19, 80-62-6; $KMnO_4$, 7722-64-7; OsO_4, 20816-12-0.

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Effects of Phenyl and Alkyl Substitutions on the Hydrogenation of Allene with Diimide

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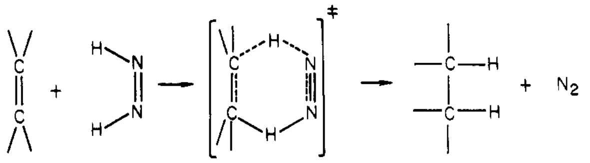
Hydrogenation of phenylpropadiene, 3-phenyl-1,2-butadiene, 1-phenyl-1,2-butadiene, and 1-phenyl-1,2-pentadiene with diimide (HN=NH) in refluxing methanol was conducted. The product distribution was analyzed as a function of reaction time, and the selectivities of the addition as well as relative reactivities were determined. Adverse steric effects of the phenyl group at the terminus of one double bond against "cis-coplanar" attack of diimide on the other double bond were found to be remarkably large. Alkyl groups activated the remote double bond of alkylallenes noticeably. This apparent electronic effect was theoretically rationalized from ab initio STO-3G model calculations of the chemical interactions.

Reactions of allenes have attracted the interest of organic chemists because of their variety in possible modes of reaction. Results of extensive work on the selectivity in addition reactions of allenes are summarized in reviews.[1-3] However, the cause of the selectivity is not well understood yet. Electronic effects of substituents were previously analyzed on the basis of NMR observations.[4] Quantitative treatments of the chemical reactivities are limited.[5,6] More precisely, a decomposition of the reactivity by each reaction mode has never been undertaken because of practical difficulties. Stepwise reactions of allenes involving allylic intermediates result in the formation of thermodynamically stable products, irrespective of kinetic selectivities; product distribution does not necessarily reflect kinetic selectivity.[7]

Contrastingly, one-step reactions give rise to the kinetically governed product distributions. For such a reaction, hydrogenation of double bonds by diimide is simple and well characterized as described in reviews.[8,9] The reaction proceeds in a concerted manner through a six-membered cyclic transition state to give a syn adduct[10] (eq 1).



(1)

In the present paper, the diimide hydrogenation of phenylpropadiene (**1a**) and its derivatives (**1b–d**) has been investigated to analyze the selectivity. Attention was focused upon the characteristic effects dependent on the structure of allene due to the mutually orthogonal cumulated double bonds. That is, how would the electronic effect of an α-substituent X be transmitted through the

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