photolysis was stopped when the amount of **4a** appeared to be at a maximum. Olefins were then removed by permanganate oxidation; **4a** (cis and trans) was isolated by column chromatography and identified by comparison (nmr and ir spectra; gc retention times) with an authentic sample of **4a** (cis and trans). We point out that this is the first isolation of **4a** from **3a** although the work of Griffin[4] left little doubt as to its being formed. Similarly, cyclopropanes **4b** (cis and trans) could be isolated from the photolysis of **3b**.[5] Strikingly, however, irradiation of **3c** led to no observable formation of **4c** or of any other product. Indeed, prolonged irradiation gave solely trans–cis isomerization with only a very slow disappearance of starting material being noted. Triplet sensitization of **3a–c** with xanthone gave only cis–trans isomerization indicating the observed migrations are singlet state processes.

Quantum yield studies of the rearrangements of the trans olefins were carried out on a merry-go-round apparatus using 254-nm light. At the low conversions (<1%) of these irradiations only trans cyclopropanes were formed.[5] The results are shown in Table I. To ensure that the differences in quantum yields found really reflected differences in singlet state reactivity rather than large rate differences in other singlet deactivation processes the quantum yields were converted to relative rates as done previously.[1,7] These are also listed in Table I.

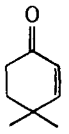
**Table I.** Quantum Yield and Relative Rate Data for Olefins **1a–c**

| Compd | $10^{-3}\varphi_r$[a] | $k_f$(rel)[b] | $\varphi_f$(rel)[b,c] | $k_r$(rel)[b] |
|---|---|---|---|---|
| **3a** | 0.0010 | 1.0 | 1.0[d] | 1.0 |
| **3b** | 0.0026 | 1.4 | 1.2[e] | 3.0 |
| **3c** | <0.0001 | 1.2 | 1.7[f] | ≤0.07 |

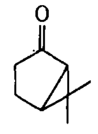
[a] ±15–20%. [b] Computed as in ref 1. [c] λ(excitation) 265 nm; solutions ~$10^{-5}$ *M* in cyclohexane. [d] $\lambda_{max}$ 313 nm. [e] $\lambda_{max}$ 318 nm. [f] $\lambda_{max}$ 329 nm.

The results are quite revealing. It is noted that—as in the rearrangement of diarylpropenes[1]—(1) substitution in the styryl group of hydrogen by a para methoxy moiety drastically curtails the rate of methyl migration, and (2) substitution by a para cyano group increases the rate though the effect here is, very interestingly, much less than with the diarylpropenes.[1] Once again we find that 1,2 migration in a $\pi-\pi^*$ state becomes less and less favorable as the electron density at the reaction terminus increases. This is notably similar to the case with ground-state 1,2 shifts of alkyl (and aryl) groups to an adjacent carbon where there is little evidence for migration of saturated carbon to other than an adjacent *cationic* center.[9] A simple picture of the photochemical case is that the reactive $\pi-\pi^*$ systems, in which a bonding orbital has lost an electron to a less stable antibonding orbital, are electrophilic in these migrations. Substituents decreasing this electrophilicity also decrease reactivity and *vice versa*.

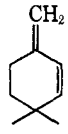
While we are exploring the generality of the effects noted here, it is worthwhile to point out their interesting connection to the relation between the reactivity of cyclohexenones and their methylene analogs.[10] 4,4-Dimethyl-2-cyclohexenone (**5**) rearranges *via* alkyl migration to bicyclic isomer **6**.[11] However, neither the singlet nor the triplet state of the methylene analog **7** of the ketone undergoes any similar sort of rearrangement.[10b] This implies[10b] (a) an $^3n-\pi^*$ state is necessary for the rearrangement or (b) it is the difference in electron distribution of the excited $\pi-\pi^*$ states that is important, that of the ketone being polarized toward oxygen. Since **5** and similar enones most likely rearrange *via* alkyl migration from $^3\pi-\pi^*$ states,[12] differences in enone and olefin excited state polarities would seem to be a possibly important factor in determining their relative reactivities.[13-15] Indeed our results with rearrangements of $\pi-\pi^*$ singlets are consistent with this and show that excited state electron distribution is very important in determining rates of migration of $\pi-\pi^*$ states.



**5**



**6**



**7**

**Acknowledgment.** We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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(7) This is essentially the procedure of Zimmerman and Baum[8a] and of Dalton and Turro.[8b]

(8) (a) H. E. Zimmerman and A. A. Baum, *J. Amer. Chem. Soc.*, **93**, 3646 (1971); (b) J. C. Dalton and N. J. Turro, *ibid.*, **93**, 3569 (1971).

(9) Reference 5, footnote 2.

(10) (a) H. E. Zimmerman and G. E. Samuelson, *J. Amer. Chem. Soc.*, **89**, 5971 (1967); H. E. Zimmerman and G. E. Samuelson, *ibid.*, **91**, 5307 (1969); (b) W. G. Dauben and W. A. Spitzer, *ibid.*, **90**, 802 (1968).

(11) O. L. Chapman, T. A. Rettig, A. I. Dutton, and P. Fitton, *Tetrahedron Lett.*, 2049 (1963).

(12) W. G. Dauben, W. A. Spitzer, and M. S. Kellogg, *J. Amer. Chem. Soc.*, **93**, 3674 (1971), and references therein.

(13) A "free rotor" effect[14] could explain the nonreactivity of the diene triplet, but most likely not that of the singlet.

(14) (a) H. E. Zimmerman and G. A. Epling, *J. Amer. Chem. Soc.*, **92**, 1411 (1970); (b) J. S. Swenton, J. A. Hyatt, T. J. Walker, and A. L. Crumrine, *ibid.*, **93**, 4808 (1971).

(15) 1,2-Alkyl shifts have been observed with acyclic diene singlets. Here, the migrating group is benzyl: E. C. Sanford and G. S. Hammond, *ibid.*, **92**, 3497 (1970).

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## The Oxidation of Cinnamic Acid by Permanganate Ion. Spectrophotometric Detection of an Intermediate

*Sir:*

Permanganate ion reacts rapidly with cinnamic acid in aqueous perchloric acid solutions to form an intermediate which appears yellow and which exhibits an absorption maximum at 415 nm. The intermediate then decomposes at a slower rate to give benzaldehyde and manganese(III) as products. Although this intermediate has only transitory existence, it has been possible to identify it and to study its rate of formation and subsequent decomposition by stopped-flow techniques.

The rate of the first step of the reaction can be determined either by following the disappearance of the permanganate ion absorption maximum at 530 nm or

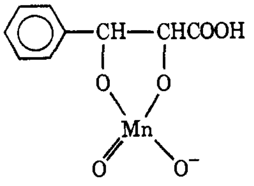
**Table I.** Isotope Effects on the Rate of Formation ($k_2$) and Decomposition ($k_1$) of the Intermediate Hypomanganate Ester During the Oxidation of *trans*-Cinnamic Acid by Acidic Permanganate[a]

| Reductant | $k_2 \times 10^{-3}$,[b] $M^{-1}$ sec$^{-1}$ | $k_2$(H)/$k_2$(D) | $k_1 \times 10^{2}$,[b] sec$^{-1}$ | $k_1$(H)/$k_1$(D) |
|---|---|---|---|---|
| *trans*-Cinnamic acid | 1.56 ± 0.03 | | 2.60 ± 0.02 | |
| *trans*-Cinnamic acid-α-*d* | 2.02 ± 0.01 | 0.77 ± 0.02 | 2.39 ± 0.02 | 1.09 ± 0.01 |
| *trans*-Cinnamic acid-β-*d* | 2.08 ± 0.01 | 0.75 ± 0.02 | 2.38 ± 0.02 | 1.09 ± 0.01 |

[a] [Reductant] = $5.23 \times 10^{-4}$ *M*, [$KMnO_4$] = $2.20 \times 10^{-4}$ *M*, [$HClO_4$] = 0.99 *M*, *T* = 30.0°. [b] The average of three or more experiments.

the appearance of the intermediate at 415 nm. Identical rates (within experimental error) are observed at both wavelengths, and the reaction is clearly second order as indicated by the excellent rate plots obtained (correlation coefficients of 0.999). The decomposition of the intermediate, which can be monitored by the decrease in absorption at 415 nm, is a somewhat slower first-order reaction.

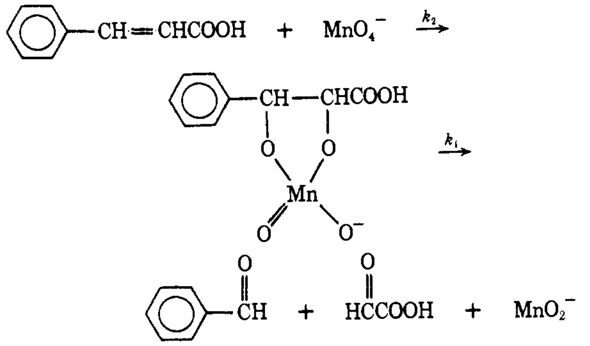
The nature of these reactions was further defined by a study of the kinetic isotope effects observed when *trans*-cinnamic acid-α-*d* and *trans*-cinnamic acid-β-*d* were used as substrates. In each case the rate of the reaction was increased by about 30% (Table I), thus suggesting that this reaction involves a rehybridization of the olefinic carbon atoms from $sp^2$ to $sp^3$.[1] The fact that an inverse isotope effect of similar magnitude was obtained at both the α and β positions indicates that the transition state is approximately symmetrical with respect to attack of the oxidant at the double bond. An attractive explanation for these observations is to suggest that the yellow intermediate is actually the hypomanganate ester **1**. Such compounds have previously been considered as intermediates in similar reactions[2,3] and the observation that the electronic spectrum has a maximum at 415 nm and a minimum around 530 nm is not inconsistent with the known spectral properties of other $Mn^V$ compounds.[3]



**1**

The second step of the reaction exhibited an isotope effect (Table I) of the magnitude usually associated with reactions where the hybridization of carbon is changed from $sp^3$ to $sp^2$.[1] Furthermore, benzaldehyde was the major detectable product of the reaction when it was carried out under an inert nitrogen atmosphere, whereas in the presence of oxygen only benzoic acid was obtained. Hence it appears that the intermediate decomposes to give, initially, benzaldehyde which then undergoes further oxidation to the product usually reported from this reaction, benzoic acid.

It was also possible to test for the presence of $Mn^{III}$ in the product solution since it is known to disproportionate to $Mn^{II}$ and $MnO_2$ under alkaline conditions.[3] When the solution of reaction products was made basic by the addition of sodium hydroxide, a brown precipitate of $MnO_2$ was indeed obtained. Hence it appears that the intermediate decomposes to give benzaldehyde and $Mn^{III}$ as the initial products. A probable sequence which accounts for all of these observations has been outlined in eq 1.



(1)

Although hypomanganate esters have often been considered as possible intermediates in these reactions,[2-4] we believe that this is the first time their physical detection has been reported. They appear to exhibit distinctly different properties from the $Mn^{III}$ intermediate which has recently been detected during the permanganate oxidation of acetylenedicarboxylic acid.[5]

The kinetics were determined in a routine way with the aid of a Durrum Model D-110 stopped-flow spectrophotometer. The preparation and identification of the deuterated cinnamic acids have been described elsewhere.[6]

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## Permanganate Oxidation of Crotonic Acid. Spectrometric Detection of an Intermediate[1]

*Sir:*

In our previous study of the kinetics of the permanganate oxidation of crotonic and cinnamic acids, evi-

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(1) This investigation was supported by the National Science Foundation.