

phorescence emission. When the 0-0 phosphorescence band was not well defined, E_T was estimated from the onset of the emission band.

As noted earlier, for convenience, substituted *n*-butyrophenones may be divided into two general groups classified as "reactive" ($\Phi_{II} \sim 0.1-0.4$) and "unreactive" ($\Phi_{II} \sim 0-0.1$).^{2,3} It is generally held that "reactive" and "unreactive" compounds possess lowest triplet states which are predominantly $^3(n, \pi^*)$ or $^3(\pi, \pi^*)$ in character, respectively.³ The *o*-, *m*-, and *p*-fluoro-*n*-butyrophenones are typical of those belonging to the "reactive" group. Methyl- and chloro-substituted compounds behave similarly. However, as seen in Table I, acetoxy and methoxy derivatives cannot be readily classified.

The Φ_{II} values for *o*- and *p*-acetoxy-*n*-butyrophenones are normal, but their phosphorescence lifetimes (τ_p) are considerably longer than those usually found for (n, π^*) triplet states. The *o*- and *p*-methoxy derivatives have lower Φ_{II} values, but τ_p is also longer than expected. The most significant result, however, is the striking decrease in Φ_{II} when acetoxy or methoxy substituents are in the position *meta* to the carbonyl group. This decrease is also accompanied by a considerable increase in τ_p , which suggests that the lowest triplet states for the *meta* derivatives are (π, π^*) states. Furthermore, the low-intensity $n \rightarrow \pi^*$ absorption, characteristic of "reactive" butyrophenones, is absent in the uv spectra of the *m*-acetoxy and *m*-methoxy compounds.

Wagner and Kempainen⁵ have found similar substituent effects for the type II cleavage of alkenes from methoxy-substituted *n*-valerophenone and γ -methylvalerophenone.

The variations in Φ_{II} are closely related to variations in G_{II} . The results emphasize the close relationship between this photochemical or radiochemical processes in solution. This can be rationalized in the following terms. In the radiolysis experiments almost all the incident energy was absorbed by the benzene solvent. Thus singlet and triplet excited states of benzene are produced initially.⁸ These subsequently transfer electronic energy to the butyrophenone, producing ultimately the lowest triplet state of butyrophenone, the acknowledged precursor to the type II process.

Our results indicate that the triplet states of acetoxy- and methoxy-*n*-butyrophenones, responsible for phosphorescence and possibly the type II reaction, have greater (π, π^*) character than those of the normal "reactive" compounds, particularly when these substituents are in the position *meta* to the carbonyl group. However, as recently pointed out,⁹ the phosphorescence emission of alkyl phenyl ketones in a matrix at 77°K has been found to consist of *both* a short- and a long-lived component.

Thus it appears that the energy separation of (n, π^*) and (π, π^*) triplet states may be quite small in certain solvents. However, the observation of short- and long-lived emissions may be caused by a matrix effect. In the case of the derivatives discussed above, although the type II reaction proceeds from a (n, π^*) triplet

state, the (π, π^*) triplet state (or a mixed triplet state) may have similar energy so that phosphorescence from both states is observed. The lack of correlation between Φ_{II} and the rate constant for hydrogen abstraction in the excited state has already been pointed out,¹⁰ and therefore the anomalous values of Φ_{II} for the *m*-methoxy and *m*-acetoxy derivatives should be cautiously interpreted, until quenching and phosphorescence data are available.

Acknowledgment. The authors are grateful to Dr. P. J. Wagner for discussion of his results prior to publication and to G. L. Dale and J. Wyatt for their assistance with the experimental work. These investigations were supported by Grant AP00109, Research Grants Branch, National Center for Air Pollution Control, Bureau of Disease Prevention and Environmental Control, U. S. Public Health Service. D. R. B. wishes to acknowledge the assistance of an Air Pollution Special Research Fellowship.

(10) J. N. Pitts, Jr., D. R. Burley, J. C. Mani, and A. D. Broadbent, *J. Am. Chem. Soc.*, **90**, 5900 (1968); P. J. Wagner and A. E. Kempainen, *ibid.*, **90**, 5896 (1968).

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Oxidation Reactions of Manganese(III) Acetate.

II. Formation of γ -Lactones from Olefins and Acetic Acid¹

Sir:

The oxidation of organic compounds by Mn(III) complexes in aqueous solution has been extensively studied, and most of the results have been successfully interpreted in terms of inner-sphere one-electron-transfer processes.² The nonaqueous chemistry has been less extensively explored,³ and the reactions previously reported have been interpreted as resulting from inner-^{3a} or outer-sphere^{3b} one-electron-transfer steps. We have found that solutions prepared by dissolving manganese(III) acetate dihydrate in glacial acetic acid react with alkanes, alkenes, and aromatic compounds to give a variety of products which are best explained as resulting from interaction of the substrate with an electrophilic species derived from solvent acetic acid or from acetate groups coordinated with the metal. In the present communication we report the formation of γ -lactones from olefins.

An example is the formation of γ -methyl- γ -phenylbutyrolactone (**2**) from α -methylstyrene (eq 1). A mixture of 360 ml of acetic acid, 180 ml of acetic anhydride, 45 g of α -methylstyrene, and 80 g of Mn(OAc)₃·2H₂O⁴ was heated to reflux (45 min) until the

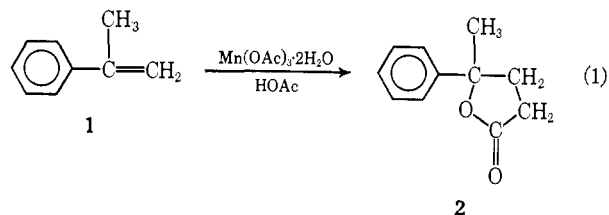
(1) Previous article in this series: H. Finkbeiner and J. B. Bush, Jr., paper presented at the Faraday Society Discussion, "Homogeneous Catalysis with Special Reference to Hydrogenation and Oxidation," University of Liverpool, Liverpool, England, Sept 1968.

(2) Reviewed by W. A. Waters and J. S. Littler in "Oxidations in Organic Chemistry," Part A, K. Wiberg, Ed., Academic Press, New York, N. Y., 1965, p 186.

(3) See, for example, (a) R. van Helden and E. C. Kooyman, *Rec. Trav. Chim.*, **80**, 57 (1961); (b) P. J. Andrusis, M. J. S. Dewar, R. Dietz, and R. L. Hunt, *J. Am. Chem. Soc.*, **88**, 5473 (1966).

(4) The Mn(OAc)₃·2H₂O was prepared by heating a mixture of 500 ml of acetic acid and 48 g of Mn(OAc)₂·4H₂O to reflux for 20 min, then slowly adding 8.0 g of KMnO₄. After refluxing for an additional 30 min, the mixture was cooled to room temperature and 85 ml of water

(8) J. M. King and G. S. Hammond, *J. Am. Chem. Soc.*, in press.
(9) N. C. Yang and S. Murov, *J. Chem. Phys.*, **45**, 4358 (1966); A. A. Lamola, *ibid.*, **47**, 4810 (1967); R. D. Rauh and P. A. Leermakers, *J. Am. Chem. Soc.*, **90**, 2246 (1968); J. N. Pitts, Jr., 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Abstracts, No. P142.



dark brown color of the Mn(III) had disappeared. After cooling to room temperature, the manganese(II) acetate was removed by filtration and the filtrate was distilled to afford 19 g (72%) of **2**, bp 104–106° (0.1 mm).

Acetic anhydride has a dramatic effect on both the rate and yield of the reaction. A repetition of the α -methylstyrene reaction in the absence of acetic anhydride required 21 hr to discharge the color and provided only a 25% yield of **2**.

The reaction of a number of other olefins has been carried out using 0.1 mol of olefin, 50 ml of acetic acid, 12 ml of acetic anhydride, and 0.05 mol of $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$. This mixture was refluxed until the Mn(III) was consumed (approximately 30–60 min), poured into 200 ml of water, extracted with ether, and analyzed by vapor phase chromatography. Table I gives the

Table I. Survey of the Formation of Lactones from Olefins

R ₁	R ₂	R ₃	R ₄	γ -Lactone ^a
C ₆ H ₅	H	H	H	39.0
C ₆ H ₅	CH ₃	H	H	30.5
C ₆ H ₅	H	CH ₃	H	21.4
C ₆ H ₅ CH ₂	H	H	H	15.8
C ₆ H ₅	H	H	C ₆ H ₅	20.0
(CH ₃) ₃ C	H	H	H	11.5
H	-(CH ₂) ₄ -		H	9.7

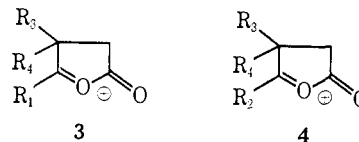
^a Yield based on $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$.

results obtained under these conditions. It should be observed that the yields do not represent optimized reaction conditions for each olefin. For example, by a slight adjustment of conditions (50 ml of AcOH, 25 ml of Ac₂O), the yield for the formation of γ -phenylbutyrolactone from styrene can be raised to 75%. Using this same set of conditions, an 83% yield of γ -methyl- γ -phenylbutyrolactone is obtained. Lactones are also formed from reactions with 1,1-diphenylethylene, 1-hexene, and 2-methyl-1-butene. No evidence for lactone formation was obtained from the reaction of 1-chloro-3,3-dimethyl-1-butene or from vinyltrimethylacetoxysilane.

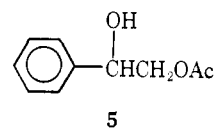
In each case, the structure proof for the lactone is based on infrared, nmr, and mass spectral data. Particularly diagnostic for the identification of samples

added. Larger amounts of water change the yield and nature of the manganese acetate and the yield of lactone on subsequent reaction with olefins. The manganic acetate was filtered off after 16 hr, washed with cold acetic acid, and air dried. The rate of reaction of manganese acetate with olefins varies somewhat with the method of preparation; however, except as previously noted, the yields are relatively unaffected. To obtain the most reactive manganese(III) acetate, we find it necessary to add acetic anhydride equivalent to the water of hydration in the manganese(II) acetate used as starting material.

trapped by vpc were the appearance of a band at 1760–1780 cm^{-1} in the infrared and the appearance of a molecular ion of the proper mass and of ions corresponding to **3** and **4** in the mass spectrum.⁵ The lactones from styrene and neohexene were also found to be identical with authentic samples.



In addition to the lactone peak in the vpc of these reaction mixtures, some other materials were identified. From cyclohexene was obtained a 22% yield of 3-acetoxycyclohexene and a 10% yield of a cyclohexenylcarbonyl acetate. An analogous product to the latter, 4,4-dimethyl-2-pentenyl acetate, was identified as a minor product from neohexene. The glycol acetate **5** constituted about 1% of the reaction mixture from styrene and manganese(III) acetate.



These results may be compared with previous reports of reactions of manganese(III) acetate with olefins. The failure of Zonis to obtain any reaction with cyclohexene and stilbene,⁶ of Julian to obtain reaction with crotonic acid or 1-nonene,⁷ and of Vieböck to obtain reaction with crotonic, itaconic, or oleic acids⁸ may have been due to the presence of water in the reaction mixtures, to failure to go to high enough temperature, or to variability in the reactivity of manganese(III) acetate.⁴ The formation of a glycol acetate from thebaine⁸ and the formation of small amounts of **5** from styrene are probably due to the presence of oxygen in the reaction mixture. Glycol esters have been previously observed as by-products of autoxidation of styrenes.^{9, 10}

The mechanisms of the reactions by which manganese(III) acetate produces lactones from olefins, brings about allylic oxidation, and causes the introduction of CH₂O or CH₂COOH groups onto aromatic rings^{1, 11} or double bonds are not yet clarified, and work is in progress concerning each of these reactions. A particularly difficult aspect of these problems has been the characterization of the manganese species present in the reaction mixture and of the role of Mn(IV) in the various reactions. Our failure to detect any polymerization of styrene in the reaction with manganese(III) acetate under conditions in which peroxide-initiated polymerization of styrene in acetic acid has been carried out¹² and the observation that manganese(III)

(5) E. Honkanen, R. Moisio, and P. Karvonen, *Acta Chem. Scand.*, **19**, 370 (1965).

(6) S. A. Zonis, *Sb. Statei Obshch. Khim.*, **2**, 1091 (1953); *Chem. Abstr.*, **49**, 5414g (1955).

(7) K. Julian, D.Sc. Thesis, University of Oxford, Sept 1962.

(8) F. Vieböck, *Chem. Ber.*, **67**, 197 (1934).

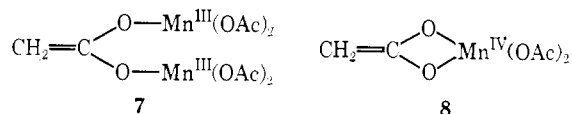
(9) F. R. Mayo and A. A. Miller, *J. Am. Chem. Soc.*, **80**, 2480 (1958).

(10) R. van Helden, A. F. Bickel, and E. C. Kooyman, *Rec. Trav. Chim.*, **80**, 1257 (1961).

(11) (a) R. E. van der Ploeg, Ph.D. thesis submitted to the Faculty of the University of Leiden, Sept 1967; (b) R. E. van der Ploeg, R. W. de Korte, and E. C. Kooyman, *J. Catalysis*, **10**, 52 (1968).

(12) V. S. Vaidhyanathan and M. Santhappa, *Makromol. Chem.*, **16**, 140 (1955).

acetate in contrast to peroxides¹³ does not cause the addition of acetate esters to olefins argue against the intervention of $\cdot\text{CH}_2\text{CO}_2\text{H}$ radicals. This radical had been suggested as being responsible for aromatic substitution brought about by manganese(III) acetate.¹¹ The nature of the products is alone insufficient evidence to rule out radical intermediates since manganese(III) has been reported to be an effective radical oxidant.¹⁴ We feel that the species responsible for lactone formation is coordinated to manganese and tentatively suggest either 7 or 8 as suitable two-electron oxidants. Kinetic evidence¹¹ indicates that the reac-



tion with aromatic hydrocarbons is first order in Mn(III), which is inconsistent with 7 or 8 and would suggest that the Mn(III) analog of 8 might be the attacking species.

Finally, we note the close relationship of the reactions reported here and the formation of γ -lactones from olefins by the oxidation of acetic acid with lead(IV) acetate.^{15, 16} The mechanism proposed for this process is inappropriate to the manganese(III) acetate reaction since we find that methane accounts for less than 2% of the manganese(III) acetate under conditions that provide a 72% yield of 2.¹⁷ If methyl radical were the species responsible for initial attack at the CH bond of acetic acid, as has been proposed for lead(IV) acetate,¹⁷ then the yields of methane and 2 should be equal.

Acknowledgment. We thank Professor E. C. Kooyman for graciously supplying us with copies of the theses of several of his students.

(13) J. C. Allen, J. I. G. Cadogan, and D. H. Hey, *J. Chem. Soc.*, 1918 (1965).

(14) L. H. Sutcliffe and J. Walkley, *Nature*, **178**, 999 (1956).

(15) E. Hahl, Ph.D. Dissertation, Technical University of Karlsruhe, 1958; cited by Criegee in ref 1, p 277.

(16) E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *J. Am. Chem. Soc.*, **90**, 2706 (1968).

(17) This result is consistent with the low yield of CH_4 reported by van der Ploeg from the reaction of manganese(III) acetate and benzene or chlorobenzene. It should be noted that the low yield of methane from these reactions indicates that the mechanism for aromatic substitution brought about by lead(IV) acetate which has been proposed by Heiba, *et al.* (E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *J. Am. Chem. Soc.*, **90**, 1082 (1968)), is not applicable to the analogous reactions with manganese(III) acetate.

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Received June 3, 1968

Oxidation by Metal Salts. IV.¹ A New Method for the Preparation of γ -Lactones by the Reaction of Manganic Acetate with Olefins

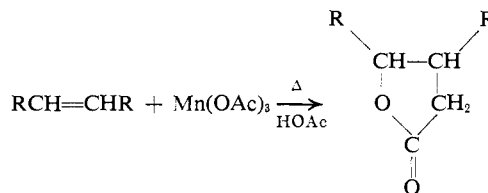
Sir:

The oxidation of olefins with lead tetraacetate and other metal acetates has been studied extensively,² but very little is known about the oxidation of olefins by manganic acetate. We now wish to report our results

(1) Part III: E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., submitted for publication.

(2) R. Criegee in "Oxidation in Organic Chemistry," Part A, K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965, p 277.

which show that manganic acetate, a readily accessible reagent,³ reacts with olefins by a free radical pathway leading to γ -butyrolactones in generally excellent yields.



In a typical experiment, a 0.1 M solution of the olefin in glacial acetic acid was refluxed under nitrogen with 2 mole equiv of $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$, in the presence of added potassium acetate (300 g/l. of HOAc),⁴ until the brown manganic color disappeared. About 1 hr is required at 135°.

Table I lists the yields of lactones obtained from various olefins under these conditions. There was no attempt made to optimize these yields, which are calcu-

Table I. Products from the Reaction of Manganic Acetate with Olefins

Olefin	Lactone	Yield, % ^c
<i>trans</i> - β -Methylstyrene		79
α -Methylstyrene		74
Octene-1		74
<i>trans</i> -Octene-4		44
Cyclooctene		62
Styrene		60
<i>trans</i> -Stilbene		16

^a Only one isomer was obtained (presumably *trans*). ^b Two isomers in the ratio of 5:1 were obtained. ^c Vpc yield based on Mn^{3+} used.

lated on the basis of Mn^{3+} consumed. The yields were generally higher, however, when based on the olefin reacted.

In a previous article we have explained the formation of lactones in the lead tetraacetate oxidation of olefins.⁵

(3) A modification of the procedure of O. T. Christiansen (*Z. Anorg. Allgem. Chem.*, **27**, 325 (1901)) was used, resulting in yields of over 80%.

(4) The high concentration of potassium acetate was used as a convenient way to raise the temperature of the refluxing solution to 135°.