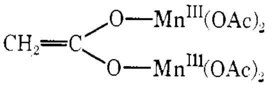
acetate in contrast to peroxides[13] does not cause the addition of acetate esters to olefins argue against the intervention of $\cdot CH_2CO_2H$ radicals. This radical had been suggested as being responsible for aromatic substitution brought about by manganese(III) acetate.[11] The nature of the products 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 evidence[11] indicates that the reaction 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.



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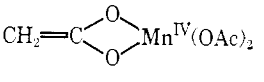

8

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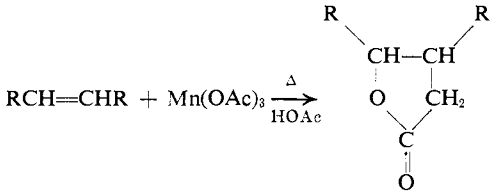
Oxidation by Metal Salts. IV.[1] A New Method for the Preparation of γ-Lactones by the Reaction of Manganic Acetate with Olefins

Sir:

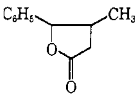
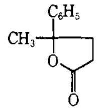
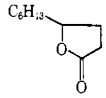
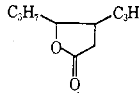
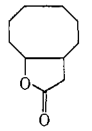
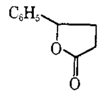
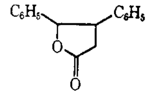
The oxidation of olefins with lead tetraacetate and other metal acetates has been studied extensively,[2] but very little is known about the oxidation of olefins by manganic acetate. We now wish to report our results which show that manganic acetate, a readily accessible reagent,[3] reacts with olefins 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 $Mn(OAc)_3 \cdot 2H_2O$, 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 calculated on the basis of Mn^{3+} consumed. The yields were generally higher, however, when based on the olefin reacted.

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

Olefin	Lactone	Yield, %[c]
trans-β-Methylstyrene		79
α-Methylstyrene		74
Octene-1		74
trans-Octene-4		44
Cyclooctene		62
Styrene		60
trans-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.

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

[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.

[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°.

The manganic acetate reaction differs from the lead tetraacetate reaction in two fundamental respects: (1) no methyl acetate adducts to β-methylstyrene are produced even at relatively high olefin concentrations, while with lead tetraacetate, under comparable reaction conditions, these adducts constituted the major isolated product; (2) only traces of CO_2 (0.03 mol/mol of Mn^{3+} consumed) and methane (0.004 mol/mol of Mn^{3+} consumed) are formed during the decomposition of manganic acetate in the presence of olefin. These differences indicate that free methyl or acetoxyl radicals are not the primary products of the thermolysis of manganic acetate in acetic acid.

We therefore propose a mechanism to account for the formation of γ-lactones similar to the one suggested for the lactone component of the lead tetraacetate reaction except that the necessary $\cdot CH_2COOH$ radicals are produced directly by thermolysis of the manganic complex.[6] The high yield of the lactones would indicate that the $\cdot CH_2COOH$ radical adds to the olefin faster than it is oxidized by Mn(III).

An expected minor side product of this reaction is the allylic acetate produced by the abstraction of an allylic hydrogen atom by the $\cdot CH_2COOH$ radical. However, the high yields of γ-lactones produced relative to the allylic acetates, ~30:1 for β-methylstyrene and ~50:1 for octene-1, clearly demonstrate the great selectivity of the $\cdot CH_2COOH$ radical toward addition to the olefin over allylic hydrogen abstraction.

The relative rate of addition of the carboxymethyl radical to various olefins was determined by applying a competitive technique and measuring the relative ratio of the lactones produced (Table II). In general the reactivity of various olefins toward the addition of the carboxymethyl radical is governed by the stability of the resulting radical intermediate. The relative rate constants of addition to *trans* and *cis* olefins are comparable to those reported for the methyl radical at 65°.[7]

Table II. Relative Reactivity of Various Olefins toward Carboxymethyl Radical Addition at 130°

α-Methylstyrene	27	Cyclooctene	0.78
1,1-Diphenylethylene	19	*cis*-Stilbene	0.36
Styrene	12	*cis*-Octene-4	0.21
2-Methylheptene-1	2.4	*trans*-Octene-4	0.20
trans-β-Methylstyrene	2.1	Styrene	1.00[b]
trans-Stilbene	1.3	*m*-Bromostyrene	1.01
cis-β-Methylstyrene	1.0	*p*-Bromostyrene	1.04
Octene-1	1.0[a]	*p*-Methylstyrene	1.26

[a] Octene-1 arbitrarily chosen as standard. [b] Styrene arbitrarily chosen as standard.

Acids other then acetic acid can be used in this reaction, thereby leading to lactones with substituents in the α position. Thus, when manganic acetate was decomposed in a solution of styrene in propionic acid containing potassium propionate, the lactone with a methyl substituent in the α position was isolated in 50% yield.[10] By analogy, manganic propionate is initially formed, which then decomposes to give the $CH_3\dot{C}H$-COOH radical.

Acknowledgment. We thank G. E. Stead and R. J. Cier for their skillful laboratory assistance.

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

[6] Recent experiments in our laboratory show that ceric acetate behaves in an analogous manner.

[7] In the additions of $\cdot CH_3$ to β-methylstyrene and stilbene $k_{trans}/k_{cis} = 2.3^8$ and 3.6^9, respectively, which are comparable to the values of 2.1 and 3.6 obtained from Table II.

[8] F. Carrock and M. Szwarc, *J. Am. Chem. Soc.*, **81**, 4138 (1959).

[9] M. Gazith and M. Szwarc, *ibid.*, **79**, 3339 (1957).

[10] The compound analyzed for $C_{11}H_{12}O_2$ and exhibited a lactone carbonyl at 5.58 μ. The nmr spectrum contained a methyl doublet at τ 9.2 (J = 6 cps) which was spin decoupled by irradiating at τ 7.75.

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Metalation Reactions. III.[1] Nuclear Magnetic Resonance Study of the Metalation of 4,5-Methylene- and 4,5-Iminophenanthrenes[2]

Sir:

In connection with a study of the electron spin resonance of dianion radicals formed by the reduction of stable hydrocarbon carbanions[1] the mechanism of metalation of weak carbon acids became of interest.[1b] Weak carbon acids react with alkali metals to produce the corresponding carbanion, the more acidic (*e.g.*, cyclopentadiene or indene) evolve hydrogen whereas others do not[1,3] (*e.g.*, fluorene or benzofluorenes).

The reduction of fluorene first produces a short-lived green color which at room temperature rapidly changes to the pale yellow color of fluorenide carbanion.[1,3] At lower temperatures the green color is stable and is due to the radical anion of fluorene.[4] The stability of the radical depends on the nature of the cation (Li > Na > K).[4] With 4,5-methylenephenanthrene the radical anion can be obtained at room temperature with sodium but not with potassium.[1b] The radical is stable if no unreacted hydrocarbon is present in solution. This observation in addition to the apparent correlation between the pK_0 of the carbon acid and the stability of the radical anion[1b] supports a proton-transfer mechanism (originally suggested by Eisch[3] in the metalation of fluorene) for the decomposition of the initially formed radical anion.

In this report we present nmr evidence for the formation of two anions in the reaction of potassium with both 4,5-methylene- and 4,5-iminophenanthrenes: the phenanthrenyl anion (I) and 9,10-dihydrophenanthrenyl anion (II). The carbanions and nitranions will be designated Ia, IIa, Ib, and IIb, respectively.

The reactions of 4,5-methylene- and 4,5-iminophenanthrenes with potassium metal were followed by

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[1] (a) E. G. Janzen and J. G. Pacifici, *J. Am. Chem. Soc.*, **87**, 5504 (1965); (b) E. G. Janzen and J. L. Gerlock, *J. Organometal Chem.* (Amsterdam), **8**, 354 (1967), should be considered parts I and II of this series.

[2] This research was supported by the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

[3] J. J. Eisch and W. C. Kaska, *Chem. Ind.* (London), 470 (1961); *J. Org. Chem.*, **27**, 3745 (1962), and references cited therein.

[4] (a) R. L. Kugel, W. G. Hodgson, and H. R. Allcock, *Chem. Ind.* (London), 1949 (1962); (b) K. A. Bilevich, N. N. Bubnov, V. V. Bukhtiyarov, and O. Y. Okhlobseptin, *Dokl. Akad. Nauk SSSR*, **174**, 594 (1967); *Proc. Acad. Sci. USSR*, **174**, 473 (1967). We have repeated this work and find the reported analyses of the fluorene radical anion spectrum in error. The values $a^{H}{}_{1,3,6,8}$ = 0.83, 1.14, $a^{H}{}_{2,7}$ = 4.82, $a_{4,5}$ = 3.99, and $a^{H}{}_{9}$ = 3.64 gauss reproduce the spectrum obtained with lithium in tetrahydrofuran and are in agreement with coupling constants obtained from spectra of 9-methyl-, 9-phenyl-, and 9,9-dimethylfluorene radical anions (to be published).