Oxidation by Metal Salts. VIII. The Decomposition of Ceric Carboxylates in the Presence of Olefins and Aromatic Hydrocarbons

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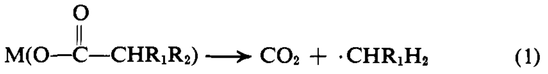
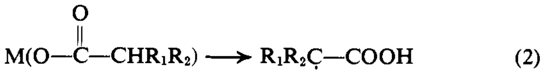
Abstract: The reactions of ceric carboxylates with olefins and aromatic hydrocarbons were used as tools for studying the decomposition mechanisms of these carboxylates. Two distinct reduction mechanisms were established: (1) a nondecarboxylative pathway involving carboxyalkyl radicals, operative in the thermal decomposition of ceric carboxylates, and (2) a decarboxylative pathway liberating alkyl radicals and carbon dioxide, which was found to be dominant in the photochemical reduction of ceric carboxylates. These reactions of ceric carboxylates with olefins and aromatic hydrocarbons were also shown to have broad synthetic utility especially for the facile preparation of γ-lactones and arylacetic acids.

During the past few years, there has been considerable interest in the thermal and photochemical decomposition of various higher valent metal carboxylates. The metal salts most thoroughly studied include those of Pb(IV),[1] Co(III),[2] Tl(III),[3] and Ce(IV).[4]

In all these cases, one general mechanism has been proposed for both the thermal and photochemical decomposition of these carboxylates. This mechanism involves the oxidative decarboxylation of the higher valent metal carboxylate with the concomitant liberation of an alkyl radical either by a concerted process or *via* the intermediacy of acyloxy radicals (eq 1, decarboxylative pathway). An alternative mode of decomposition has recently been demonstrated in the thermal decomposition of manganic carboxylates[5–7] which involves the formation of carboxyalkyl radicals in a nondecarboxylative process (eq 2, carboxyalkyl radical pathway (nondecarboxylative)).



$$M(O-\overset{\overset{\displaystyle O}{\|}}{C}-CHR_1R_2) \longrightarrow CO_2 + \cdot CHR_1H_2 \qquad (1)$$

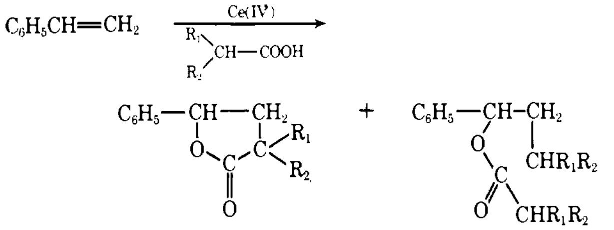


$$M(O-\overset{\overset{\displaystyle O}{\|}}{C}-CHR_1R_2) \longrightarrow R_1R_2\underset{\cdot}{C}-COOH \qquad (2)$$

In order to elucidate the decomposition mechanism of ceric carboxylates, both the thermal and photochemical reactions were studied in the presence of various olefins and aromatic hydrocarbons. These studies indicated that the thermal and photochemical decomposition mechanisms of ceric acetate were not identical, contrary to what was previously suggested.[4] These oxidation reactions of olefins and aromatic hydrocarbons were found to be not only excellent tools for distinguishing the various carboxylate reduction mechanisms but also reactions of broad synthetic utility.

Results

Reactions of Ceric Carboxylates with Olefins. Ceric acetate, prepared by ozonolysis,[8] and a large excess of styrene (~1.5 *M*) were heated in glacial acetic acid containing 10% potassium acetate at 110° for 20 hr. The major product obtained was the lactone Ia in 70% yield based on the ceric ion consumed, assuming the requirement of 2 equiv of cerium (IV) per mole of lactone. Essentially no ester IIa (<0.2% yield) was observed.



Ia, $R_1 = R_2 = H$
Ib, $R_1 = CH_3$; $R_2 = H$
Ic, $R_1 = R_2 = CH_3$

IIa, $R_1 = R_2 = H$
IIb, $R_1 = CH_3$; $R_2 = H$
IIc, $R_1 = R_2 = CH_3$

When propionic acid containing 10% sodium propionate was used in place of acetic acid, the corresponding lactone Ib (consisting of two isomers in about a 2:1 ratio) was obtained in 60% yield, and again essentially no ester IIb (<0.2%) was formed.

When isobutyric acid containing 10% sodium isobutyrate was used, only a low yield (~3%) of the lactone Ic was obtained together with some of the ester IIc (~1%).

In all these reactions rapid exchange of carboxylate ligands with ceric acetate was assumed.

Reactions of Lead Tetraacetate with Olefins. The corresponding reactions of lead tetraacetate with 1.5 *M* styrene under comparable conditions resulted in the predominant formation of the esters IIa, IIb, and IIc. The relative amount of lactone formed was less than 1% of the ester with either acetic acid or propionic acid,

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[1] (a) J. K. Kochi, *J. Amer. Chem. Soc.*, 87, 3609 (1965); (b) J. K. Kochi, J. D. Bacha, and T. W. Bethea, *ibid.*, 89, 6538 (1967); (c) J. K. Kochi, R. A. Sheldon, and S. S. Lande, *Tetrahedron*, 25, 1197 (1969).

[2] (a) A. Clifford and W. Waters, *J. Chem. Soc.*, 2796 (1965); (b) T. Cooper, A. Clifford, D. Mills, and W. Waters, *ibid.*, *B*, 793 (1966); (c) S. S. Lande and J. K. Kochi, *J. Amer. Chem. Soc.*, 90, 5196 (1968).

[3] J. K. Kochi and T. W. Bethea, *J. Org. Chem.*, 33, 75 (1968).

[4] R. A. Sheldon and J. K. Kochi, *J. Amer. Chem. Soc.*, 90, 6688 (1968).

[5] E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *ibid.*, 90, 5905 (1968).

[6] E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *ibid.*, 91, 138 (1969).

[7] R. E. van der Ploeg, R. W. deKorte, and E. C. Kooyman, *J. Catal.*, 10, 52 (1968).

[8] N. Hay and J. K. Kochi, *J. Inorg. Nucl. Chem.*, 30, 884 (1968).

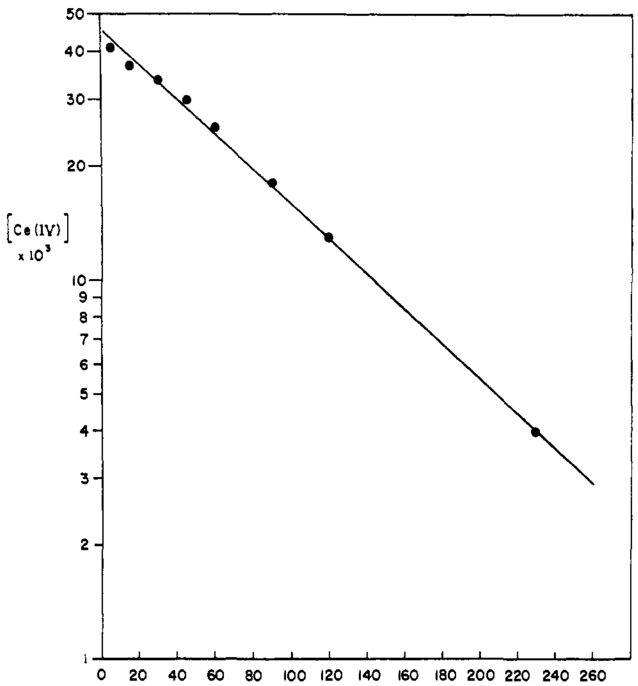


Figure 1. Kinetics of Ce(IV) reduction in 10% KOAc–acetic acid at 110°; 0.5 *M* octene-1.

and less than 6% of the ester in the case of isobutyric acid (see Table I).

Table I. Product Yields in the Thermal Decomposition of Ceric and Lead Carboxylates in the Presence of Styrene (1.5 *M*)

Acid[a]	Oxidant	Lactone yield, %	Ester yield, %
Acetic	Ce(IV)	70	<0.2
Acetic	Pb(IV)	<0.4	37
Propionic	Ce(IV)	60	<0.2
Propionic	Pb(IV)	<0.5	52
Isobutyric	Ce(IV)	~3	~1
Isobutyric	Pb(IV)	1	23

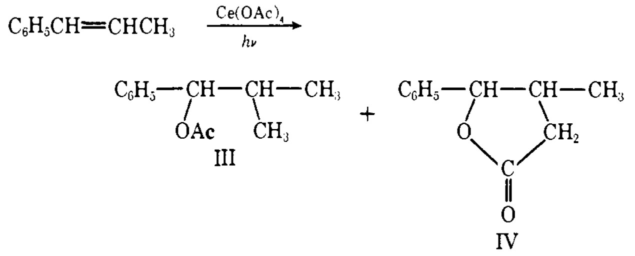
[a] 10% sodium carboxylate added in all reactions.

Reaction of Ceric Ammonium Nitrate with Olefins. For the synthetic preparation of lactones, the commercially available $Ce(NH_4)_2(NO_3)_6$ can be used in place of ceric acetate. For example, the reaction of ceric ammonium nitrate with octene-1 in glacial acetic acid containing 30% potassium acetate gave a 55% yield of γ-*n*-hexylbutyrolactone.

Table II. Product Ratios in the Photochemical Decomposition of Ceric Acetate and Lead Tetraacetate in the Presence of Olefins

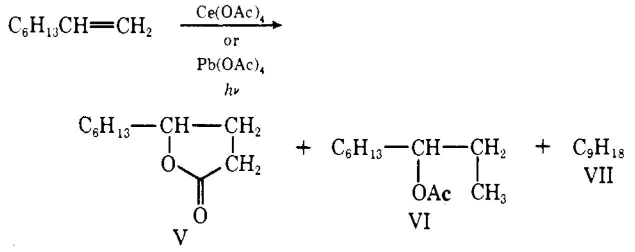
[Olefin]	Oxidant	Lactone IV/ester III
0.2 *M trans*-β-methylstyrene	Ce(IV)	0.23
0.4 *M trans*-β-methylstyrene	Ce(IV)	0.11
0.2 *M trans*-β-methylstyrene	Pb(IV)	0.23
0.4 *M trans*-β-methylstyrene	Pb(IV)	0.10

Photochemical Reaction of Ceric Acetate and Lead Tetraacetate with Olefins. In contrast to the thermal reaction of ceric carboxylates with olefins, the photochemical reaction in Pyrex at 30° produced significant quantities of ester relative to lactone. When 0.2 *M trans*-β-methylstyrene was used as the olefin, the major product observed was the ester III in 77% yield. The total yield of ester and lactone was 95% based on the ceric ion used (see Table II).



The photochemical reaction of ceric acetate paralleled that of lead tetraacetate which produced essentially the identical product distributions under the same reaction conditions. In both cases, the ratio of ester III to lactone IV doubled as the olefin concentration was increased from 0.2 to 0.4 *M*.

The similarity in product distributions obtained in the photochemical reactions of ceric acetate and lead tetraacetate was also observed when 0.2 *M* octene-1 was used as the olefin. In this reaction, three major products were produced: the lactone V, the ester VI, and nonene VII. The ratio of lactone to the sum of ester and nonene obtained was 1.23 in the case of ceric acetate and 1.28 with lead tetraacetate.

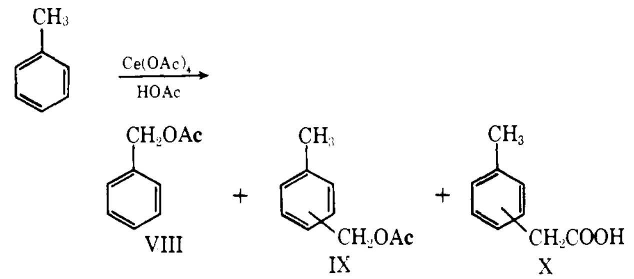


Kinetic Data. The rates of reduction of ceric acetate in the presence of various concentrations of olefins such as α-methylstyrene or octene-1 were determined by iodometric titration. Linear first-order plots were obtained for better than 90% reaction (Figure 1). The reaction rate was found to be first order in ceric acetate and independent of the olefin concentration or the nature of the olefin. The rate constants derived are shown in Table III.

Table III. Observed First-Order Rate Constants for the Reduction of Ceric(IV) Acetate in the Presence of Olefins

[Olefin]	k, sec^{-1}
0.2 *M* octene-1	1.68×10^{-4}
0.5 *M* octene-1	1.74×10^{-4}
0.25 *M* α-methylstyrene	1.77×10^{-4}

Reaction of Ceric Acetate with Toluene. The reaction of ceric acetate with toluene in glacial acetic acid produced three major products: benzyl acetate (VIII), methylbenzyl acetate (IX), and tolylacetic acid (X).



A typical experiment, 4.84 mmol of Ce(OAc)$_4$ heated at 110° in a solution of 6.4 g of toluene and 10 ml of acetic acid, yielded 0.28 mmol of benzyl acetate, 0.31 mmol of methylbenzyl acetate, and 0.45 mmol of tolylacetic acid, thereby accounting for 56% of the ceric acetate used.[9]

Reaction of Ceric Acetate with Aromatic Hydrocarbons. Synthesis of Arylacetic Acids. When the reaction of ceric acetate with toluene was run in acetic anhydride–acetic acid containing 10% potassium acetate, no methylbenzyl acetate was formed, the only two major products being benzyl acetate and tolylacetic acid. These modified reaction conditions were ideally suited for the simple one-step preparation of arylacetic acids from aromatic hydrocarbons. A few examples are shown in Table IV.

Table IV. Ceric Acetate Synthesis of Acrylacetic Acids

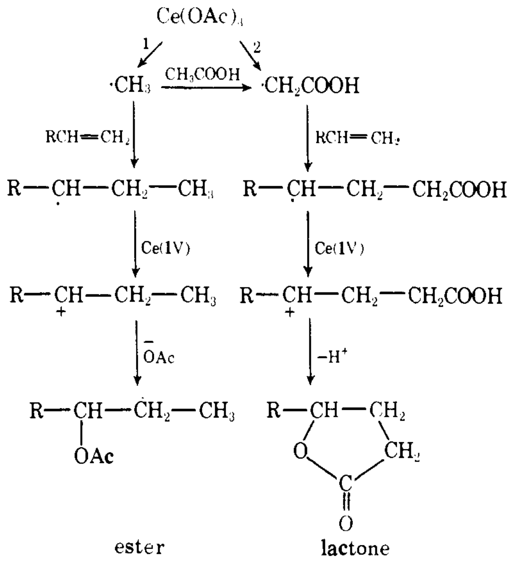
Aromatic hydrocarbon	Yield of acid,[a] %
Benzene	41
Toluene	29[b]
Chlorobenzene	36

[a] Yields were based on ceric ion, assuming 2 equiv/mol of acids produced. [b] Benzyl acetate was also produced.

Discussion

The Reaction of Ceric Carboxylates with Olefins. The formation of lactones and esters has previously been observed in the decomposition of manganic[5,10] and lead[11,12] carboxylates in the presence of various olefins. The free-radical mechanism proposed for the formation of these products is shown in Scheme I. In general, two distinct modes of metal carboxylate decomposition have been observed: (1) a decarboxylative pathway resulting in the generation of an alkyl radical (eq 3) and (2) a nondecarboxylative pathway leading directly to the formation of carboxyalkyl radicals (eq 4). Only the first pathway results in the formation of esters, whereas lactones may be obtained *via* either process, since both processes produce carboxyalkyl radicals, one indirectly and the other directly. If the first process is operative, the relative yield of lactone to ester should also be dependent on the relative concentration of the olefin and its reactivity toward free-radical addition, as was observed in the case of lead tetraacetate.[11] Furthermore, if the decomposition is carried out in the presence of high concentrations of a very reactive olefin, the decarboxylative process would lead exclusively to the ester, whereas the nondecarboxylative pathway would produce, exclusively, lactone.

Scheme I



$$\mathrm{Ce(OAc)_4} \longrightarrow \mathrm{CH_3\cdot} + \mathrm{CO_2} + \mathrm{Ce(OAc)_3}$$
$$\mathrm{CH_3\cdot} + \mathrm{CH_3COOH} \longrightarrow \mathrm{\cdot CH_2COOH} + \mathrm{CH_4} \qquad (3)$$

$$\mathrm{Ce(OAc)_4} \longrightarrow \mathrm{\cdot CH_2COOH} + \mathrm{Ce(OAc)_3} \qquad (4)$$

The Thermal Decomposition of Ceric Acetate. The thermal decomposition of ceric carboxylates at 110° was investigated in the presence of 1.5 *M* styrene. Under these conditions, the thermal decomposition of lead tetraacetate in either acetic acid or propionic acid yielded less than 1% lactone relative to the ester, which was obtained as the major product. Since the decomposition of lead tetraacetate is known to follow the decarboxylative pathway,[1,11,12] the low relative yield of lactone here indicated the essentially complete trapping of the alkyl radical by styrene.

Under identical conditions, the thermal decomposition of ceric acetate and ceric propionate resulted in high yields of lactones (60–70% based on ceric ion consumed), together with only trace amounts (<0.2%) of the corresponding esters. The high yields of lactones formed in these reactions clearly demonstrate that the predominant, if not exclusive mode of thermal decomposition of primary ceric carboxylates, is the second nondecarboxylative pathway involving the direct formation of carboxyalkyl radicals. Undoubtedly, the same decomposition mechanism operates in the absence of olefins, since the rate of ceric acetate reduction was found to be first order in ceric ion only and totally independent of the nature or concentration of the added olefin (Table III).

The thermal decomposition of secondary ceric carboxylates, such as ceric isobutyrate, apparently also follows the second pathway to a large extent. This is indicated by the observation that the yield of lactone, albeit low, obtained from ceric isobutyrate exceeded that of the ester, whereas in the corresponding lead(IV) reaction the lactone yield was less than 6% of the ester yield. The low yield of lactone obtained from ceric isobutyrate may be due to the greater ease of oxidation

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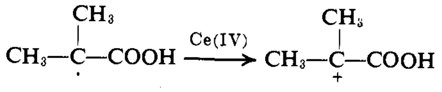
[9] This calculation is based on the stoichiometry of 2 mol of ceric acetate/mol of VIII and X, and 4 mol of ceric acetate/mol of IX obtained.

[10] J. B. Bush, Jr., and H. Finkbeiner, *J. Amer. Chem. Soc.*, **90**, 5903 (1968); *Discuss. Faraday Soc.*, **46**, 150 (1968).

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

[12] R. O. C. Norman and C. B. Thomas, *J. Chem. Soc. B*, 771 (1967); 994 (1968).

of the tertiary carboxyalkyl radical by ceric ion as well as its lower reactivity toward addition to olefins.



$$\mathrm{CH_3{-}\overset{\displaystyle CH_3}{\underset{\cdot}{C}}{-}COOH \xrightarrow{Ce(IV)} CH_3{-}\overset{\displaystyle CH_3}{\underset{+}{C}}{-}COOH}$$

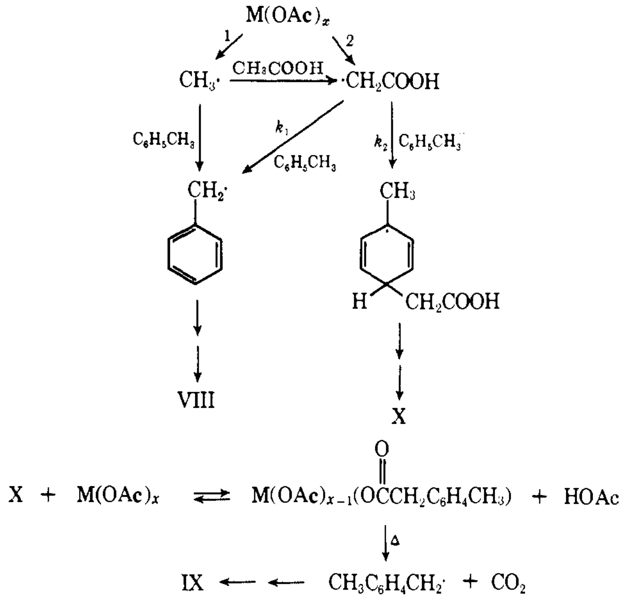
The decomposition of tertiary ceric carboxylates such as ceric pivalate obviously can only proceed *via* the first decarboxylative path since the second pathway requires the availability of α-hydrogen atoms.

The Photochemical Decomposition of Ceric Acetate. In contrast to the thermal decomposition of ceric acetate, the photochemical reduction ($\lambda \sim 3600$ Å, 30°) proceeds predominantly *via* the decarboxylative pathway. This is indicated by the similarity in product distributions obtained in the photochemical reactions of ceric acetate with those of lead tetraacetate (Table II) which are known to follow the decarboxylative process.[1] The formation of esters as major products in the photochemical reactions of ceric acetate with β-methylstyrene or octene-1 resulted from the addition of methyl radicals to the olefins. As expected on the basis of the mechanism depicted in Scheme I, the ratio of lactone to ester decreased as the olefin concentration increased. The five–sixfold increase in the lactone to ester ratio observed in going from 0.2 *M* *trans*-β-methylstyrene to 0.2 *M* octene-1 merely reflects the greater radical-trapping ability (methyl affinity) of the β-methylstyrene.[13]

The dramatic difference in mechanism between the photochemical and thermal reductions of ceric carboxylates demonstrates the necessity of studying these reactions in the presence of radical traps such as olefins. The decomposition of ceric carboxylates has previously been studied in the absence of olefins[4] and it was concluded that the thermal and photochemical decompositions were equivalent in that they both proceeded by decarboxylation and liberation of alkyl radicals. That conclusion was based on the observation of CO_2 and products derived from the alkyl radicals. However, it is most significant that in the photochemical decomposition of ceric carboxylates, the reported yield of CO_2 (65–97%) and products derived from alkyl radicals (50–90%) were considerably higher than those obtained in the thermal decomposition (9–12% CO_2, 3–8% products derived from radical intermediates). The observation of low yields of CO_2 is poor evidence for the decarboxylative pathway since the nondecarboxylative pathway yields some CO_2 from the subsequent decarboxylation of acetoxyacetic as was reported for the decomposition of manganic acetate.[6] The observed difference in the yield of products obtained in the thermal and photochemical decomposition is quite consistent with our observation of two distinct modes of reduction in the two instances.

The Reaction of Ceric Acetate with Toluene. The thermal decomposition of ceric acetate in the presence of toluene yielded three major products: benzyl acetate (VIII), methylbenzyl acetate (IX), and tolylacetic acid (X). The mechanism of formation of these products in the case of lead tetraacetate,[14] *via* methyl radicals resulting from decarboxylative decomposition, and in the case of manganic acetate,[6] *via* carboxymethyl radicals formed directly in a nondecarboxylative process, has already been adequately demonstrated (Scheme II).

Scheme II



The similarity in the product distributions obtained with ceric acetate and with manganic acetate[6] (see Table V), which differed considerably from that observed under the same conditions using lead tetraacetate,[14] confirmed the nondecarboxylative mode of ceric acetate thermolysis and the intermediacy of free carboxymethyl radicals. The product ratio VIII/(IX + X) in the ceric acetate reaction reflects the relative rates of side-chain (k_1) and nuclear (k_2) attack by the carboxymethyl radical on toluene, and is comparable to the value obtained in the manganic acetate reaction. The approximately threefold greater rate of nuclear addition relative to α-hydrogen abstraction by the carboxymethyl radical is also consistent with the data obtained from the lead tetraacetate reaction by extrapolation to infinite toluene dilution.[14]

Table V. Product Ratios Obtained in the Thermal Decomposition of Various Metal Acetates in the Presence of Toluene

Metal acetate	VIII/(IX + X)
$Ce(OAc)_4$	0.37[a]
$Mn(OAc)_3$	0.3[a,b]
$Pb(OAc)_4$	2.0[a,c]
$Pb(OAc)_4$	0.27[c,d]

[a] $[C_6H_5CH_3]/[CH_3COOH] = 0.4$, $T = 110°$. [b] Reference 6. [c] Reference 14. [d] Value obtained by extrapolation to infinite toluene dilution.

The Synthesis of Arylacetic Acids by the Reaction of Ceric Acetate with Aromatic Hydrocarbons. One major difference observed in comparing the ceric and manganic acetate reactions was the relatively high ratio of tolylacetic acid (X) to methylbenzyl acetate (IX) formed in the ceric reaction. For example, when an acetic anhydride–acetic acid solution containing 10% potassium acetate was used, no methylbenzyl acetate was observed and the isomeric tolylacetic acids were the only products obtained. Since the methylbenzyl ace-

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(13) F. Carrock and M. Szwarc, *J. Amer. Chem. Soc.*, 81, 4138 (1959).

(14) E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *ibid.*, 90, 1082 (1968).

tate is a secondary product derived by oxidation of the initially formed tolylacetic acid (Scheme II), the high relative yield of tolylacetic acid suggests that the rate of carboxylate substitution on Ce(IV) may be a relatively slow process compared to the rate of reduction under these conditions. A possible role of acetic anhydride in increasing the yield of arylacetic acids may by due to the trapping of the initially formed acids in the form of oxidatively stable mixed anhydrides.[15]

This reaction, therefore, is ideally suited for the simple one-step preparation of arylacetic acids from aromatic hydrocarbons. A few representative examples are shown in Table IV. Arylacetic acid yields were in the 30–40% range based on ceric ion consumed. No attempt was made, however, to maximize these yields. The lower yields here as compared to the lactone synthesis merely reflect the poorer radical trapping ability of the aromatic hydrocarbons relative to reactive olefins such as styrene. Nevertheless, the simple nature of this one-step reaction, as well as the absence of significant side products, makes this reaction practical for the synthesis of arylacetic acids.

Experimental Section

Preparation of Ceric(IV) Acetate. Ceric acetate was prepared by ozonolysis of cerous acetate in the presence of nitrate ion by the method of Hay and Kochi.[8] Ceric acetate was obtained as a stable yellow solid, relatively insoluble in glacial acetic acid ($<7 \times 10^{-3}$ *M* but 0.05 *M* in the presence of 10% KOAc at room temperature). Analysis by iodometric titration indicated 99% $Ce(OAc)_4$.

Thermal Reactions of Ceric Carboxylates with Styrene. In a typical experiment, 10 g of styrene (freshly distilled), 50 ml of the appropriate acid, 5 g of sodium carboxylate, and 2.5 mmol of ceric acetate were placed in a glass tube and flushed with nitrogen. The tube was then sealed tightly with a rubber septum and placed in a 110° constant-temperature bath. At this temperature, ceric acetate was entirely in solution. After approximately 5–20 hr, the tubes were cooled and opened, and an internal standard (2-methylnaphthalene) was added. The reaction mixture was diluted with 500 ml of ether and washed twice with 1 l. of ice water. The ether layer was extracted twice with saturated aqueous sodium bicarbonate to remove all traces of acid. The ether extract was then dried over sodium sulfate, filtered, and concentrated on a rotary evaporator.

The residue was analyzed by vapor phase chromatography on an F&M Model 810 gas chromatograph with dual flame detectors. The columns used were a 12 ft × 0.25 in. 5% silicone OV-17, a 12 ft × 0.25 in. 5% silicone SE-30, and a 6 ft × 0.25 in. 10% cyanoethyl silicone AN-600. Peak areas were measured with a Varian Aerograph Model 475 automatic integrator, and peak responses were calibrated with mixtures prepared from authentic samples.

Authentic samples of the various esters and lactones were available from previous studies with lead tetraacetate and manganic acetate. The structures of these compounds were definitely established by elemental analyses, as well as by infrared, nmr, and mass spectroscopy.

Preparation of Lactones Using Ceric Ammonium Nitrate. A mixture of 60 g of KOAc and 200 ml of glacial acetic acid was heated to reflux under a nitrogen atmosphere. Octene-1 (2.2 g; 20 mmol), followed by 23.6 g of $Ce(NH_4)_2(NO_3)_6$ (40 mmol), was then added. After 0.5 hr, the reaction mixture was cooled and worked up in the usual manner. The yield of γ-*n*-hexylbutyrolactone was 55% (vpc).

Photochemical Reactions of Ceric Acetate with Olefins. An acetic acid solution, 0.2 or 0.4 *M* in *trans*-β-methylstyrene or octene-1, 0.043 *M* in $Ce(OAc)_4$, and 1 *M* in KOAc, was purged with nitrogen and sealed in a Pyrex tube. The sealed tube was immersed in a 30° water bath and irradiated by a 550-W high-pressure mercury vapor lamp (Hanovia no. 673A-36) at a distance of 1–2 in. After 2–3 hr of irradiation, by which time the ceric ion was completely reduced, the tubes were opened, and the reaction mixture worked up by extraction in the usual manner. Product ratios were determined by vapor phase chromatography, after calibration with authentic samples.

The corresponding reactions of lead tetraacetate (0.021 *M*) were performed in the identical manner.

Kinetic Experiments. The rates of reduction of ceric acetate in the presence of olefins were determined by iodometric titration. In a typical experiment, 100 ml of an acetic acid solution 4.6×10^{-2} *M* in ceric acetate, 1 *M* in KOAc, and 0.2 *M* in octene-1, was placed in a reactor maintained at 110° by refluxing toluene vapors. A constant slow stream of nitrogen was passed through the solution, which was protected from light by aluminum foil. Samples (5 ml) were withdrawn periodically and titrated iodometrically.

Reactions of Ceric Acetate with Toluene. In a typical experiment, 6.4 g of toluene, 10 ml of glacial acetic acid, and 4.84 mmol of $Ce(OAc)_4$ were placed in a tube and the reaction mixture was flushed with nitrogen before the tube was sealed. The sealed tube was placed in a 110° constant temperature bath for 17 hr, by which time all the ceric ion had reacted. When an internal standard was desired, 100 mg of methyl benzoate was added to the cooled reaction mixture. The reaction mixture was diluted with 500 ml of ether and 1 l. of ice water. After separation of the two layers, the ether layer was extracted with four 500-ml portions of water. The ether extract was dried over sodium sulfate, filtered, and concentrated on a rotary evaporator.

The residue was analyzed by vapor phase chromatography on a 12 ft × 0.25 in. 15% silicone SE-30 column with temperature programming (100–300° at 10°/min). Only three major products were observed: benzyl acetate, methylbenzyl acetate, and tolylacetic acid. Accurate quantitative analysis of the tolylacetic acid required its conversion to the trimethylsilyl derivative. This was accomplished in the following way: 0.5 ml of *N*,*O*-bis(trimethylsilyl)-acetamide (BSA, Pierce Chemical Co.) was injected into a stoppered vial containing 0.5 ml of the reaction residue. After standing for 5 min at room temperature, the resulting solution was analyzed by vpc. Larger amounts of BSA or longer standing times did not affect the analyses. These analyses, after calibration with authentic samples, indicated the presence of 0.28 mmol of benzyl acetate, 0.31 mmol of methylbenzyl acetate, and 0.45 mmol of tolylacetic acid, thereby accounting for 56% of the ceric ion used.

Ceric Acetate Synthesis of Arylacetic Acids. Anhydrous 1 *M* potassium acetate–acetic acid solution was prepared by refluxing 98 g of KOAc, 900 ml of glacial acetic acid, and 100 ml of acetic anhydride overnight.

As a representative example, 3.9 g of benzene, 4.84 mmol of ceric acetate, and 50 ml of the above solution were placed in a tube and flushed with nitrogen. The tube was then sealed and placed in a 110° constant temperature bath for 18 hr. The reaction mixture was worked up as in the preceding example and similarly treated with BSA. Vpc analysis, with internal standard, indicated the presence of only one major product, phenylacetic acid, in 41% yield, based on ceric ion used.

Acknowledgment. The skillful technical assistance of Messrs. R. J. Cier and G. E. Stead is gratefully acknowledged.

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[15] This idea was suggested by one of the referees.