

# Oxidation of Organic Compounds with Cerium(IV). XVIII. Oxidative Decarboxylation of Substituted Phenylacetic Acids<sup>1</sup>

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**Abstract:** Substituted phenylacetic acids are readily decarboxylated when treated with ceric ammonium nitrate in aqueous acetonitrile solutions containing nitric acid to give carbon dioxide and the corresponding benzyl alcohol, benzaldehyde, and benzyl nitrate. Oxygen-trapping experiments indicate that benzyl radicals are formed as intermediates. A Hammett plot of the relative rates of oxidation of meta- and para-substituted phenylacetic acids vs.  $\sigma^+$  values gave a  $\rho$  of  $-2.91 \pm 0.29$ . The oxidative decarboxylation is proposed to be a one-electron process with the rate-determining step being the decomposition of a carboxylic acid-cerium(IV) complex to a benzyl radical and carbon dioxide through a very polar transition state.

The oxidative decarboxylation of carboxylic acids has been studied extensively. Many of the oxidants used for this reaction are metallic ones such as lead(IV),<sup>2</sup> cobalt(III),<sup>3</sup> silver(II),<sup>4</sup> manganese(III),<sup>5</sup> thallium(III),<sup>6</sup> and chromic acid,<sup>7</sup> but nonmetallic oxidants<sup>8</sup> have also been used. In addition, oxidative decarboxylations have been effected electrolytically.<sup>9</sup>

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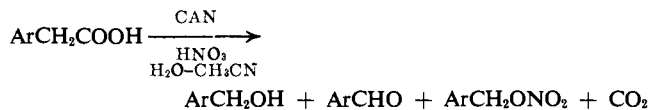
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Sheldon and Kochi<sup>10</sup> studied the oxidative decarboxylation of a series of cerium carboxylates both photochemically and thermally. Only aliphatic acids were studied and they were used in excess as the solvent for the oxidation. For the photochemical reaction, it was concluded that the initial process involves formation of acyloxy radicals. In the thermal reaction, it was felt that formation of the alkyl radical occurs directly.



The cerium(IV) perchlorate oxidation of acetic acid was studied by Mathai and Vasudevan<sup>11</sup> and evidence for a cerium-acetic acid complex was obtained.

We have found that phenylacetic acids are readily decarboxylated when treated with ceric ammonium nitrate (CAN) in aqueous acetonitrile containing nitric acid to give carbon dioxide and the corresponding benzyl alcohol, benzaldehyde, and benzyl nitrate. This system permits the determination of substituent



effects on the rate of this reaction since a variety of ring-substituted phenylacetic acids can be studied and the reaction is facile enough that a large excess of carboxylic acid is not required.

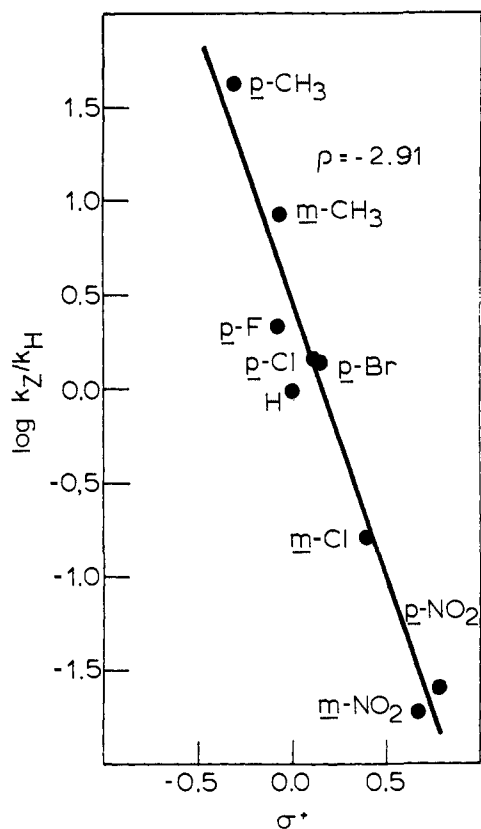
## Results

Treatment of *p*-methylphenylacetic acid (0.4 M) with 2.2 equiv of CAN in a 30% aqueous acetonitrile solution containing nitric acid (0.35 M) for 2 min at 90° gave 42% *p*-methylbenzyl alcohol, 19% *p*-methylbenzaldehyde, 5% *p*-methylbenzyl nitrate, and 20% starting material. Analysis of the gas from the CAN oxidation of *p*-methylphenylacetic acid in 70% aqueous aceto-

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(11) I. M. Mathai and R. Vasudevan, *J. Chem. Soc. B*, 1361 (1970).



**Figure 1.** Plot of the logarithms of the relative rates of oxidative decarboxylation of phenylacetic acids by CAN vs.  $\sigma^+$  values of the substituents.

nitrile containing nitric acid (0.35 M) gave an 80% yield of carbon dioxide.

The relative rates of oxidative decarboxylation of a series of substituted phenylacetic acids were measured by competition studies. Two acids were accurately weighed into a flask and solvent was added. A CAN solution in the same solvent was added and the mixture was heated on a steam bath until the color of the solution became pale yellow or colorless. A limited amount of CAN was used so that some of both carboxylic acids remained at the end of the reaction. The amount of each acid remaining was determined by nmr analysis. With the assumptions that the oxidation of a carboxylic acid by cerium(IV) proceeds through a complex<sup>11</sup> and that there is negligible effect on the equilibrium constants for complex formation by the substituent, the relative rates of decomposition of the complexes are given by

$$k_x/k_y = [\log (X_0/X_f)/\log (Y_0/Y_f)]$$

where  $X_0$  and  $X_f$  are the initial and final concentrations of acid X and  $Y_0$  and  $Y_f$  are the initial and final concentrations of acid Y. The assumption that the formation constants for the complexes are equal is a reasonable one since the  $pK_a$  values for substituted phenylacetic acids vary only slightly, ranging from 3.92 for the *p*-nitro acid to 4.36 for *p*-methoxy- and *p*-methylphenylacetic acid.<sup>12</sup> Moreover, Smith and Waters<sup>3e</sup> have determined that the equilibrium constants for complex formation in the cobalt(III) oxida-

(12) A. Fischer, B. R. Mann, and J. Vaughan, *J. Chem. Soc.*, 1093 (1961).

tion of propionic and phenylacetic acids are essentially the same and the formation constants of alcohol-cerium(IV) complexes have been found to be not unusually sensitive to electronic effects.<sup>13</sup> The results of these competitive oxidations for 11 acids are presented in Tables I and II.

**Table I.** Competitive Rates of CAN Oxidation of Substituted Phenylacetic Acids,  $ZC_6H_4CH_2COOH$ , in 30% Aqueous Acetonitrile<sup>a</sup>

Competing phenylacetic acids, $Z_1/Z_2$	Competitive rates, $k_1/k_2$
<i>p</i> -CH <sub>3</sub> O/ <i>p</i> -CH <sub>3</sub>	> 50 <sup>b</sup>
<i>m</i> -CH <sub>3</sub> O/ <i>p</i> -CH <sub>3</sub>	> 50 <sup>c</sup>
<i>p</i> -CH <sub>3</sub> / <i>p</i> -Cl	28.6 ± 8.5 <sup>b</sup>
<i>m</i> -CH <sub>3</sub> /H	8.50 ± 0.31 <sup>d</sup>
<i>m</i> -CH <sub>3</sub> / <i>p</i> -F	3.86 ± 0.30 <sup>b</sup>
<i>p</i> -Cl/H	1.48 ± 0.04 <sup>b</sup>
<i>p</i> -Br/H	1.44 ± 0.07 <sup>d</sup>
H/ <i>m</i> -Cl	5.97 ± 0.34 <sup>e</sup>
<i>m</i> -Cl/ <i>p</i> -NO <sub>2</sub>	6.21 ± 1.15 <sup>d</sup>
<i>m</i> -Cl/ <i>m</i> -NO <sub>2</sub>	8.76 ± 0.43 <sup>d</sup>

<sup>a</sup> Containing 0.35 M nitric acid at 90°. <sup>b</sup> Based on five runs. <sup>c</sup> Based on one run. <sup>d</sup> Based on four runs. <sup>e</sup> Based on three runs.

**Table II.** Relative Rates of CAN Oxidation of Substituted Phenylacetic Acids,  $ZC_6H_4CH_2COOH$ , in 30% Aqueous Acetonitrile<sup>a</sup>

Z	$k_z/k_H$
<i>p</i> -CH <sub>3</sub> O	> 2000
<i>m</i> -CH <sub>3</sub> O	> 2000
<i>p</i> -CH <sub>3</sub>	42.3 ± 12.6
<i>m</i> -CH <sub>3</sub>	8.50 ± 0.31
<i>p</i> -F	2.20 ± 0.19
<i>p</i> -Cl	1.48 ± 0.04
<i>p</i> -Br	1.44 ± 0.07
H	(1.00)
<i>m</i> -Cl	0.168 ± 0.010
<i>p</i> -NO <sub>2</sub>	0.0270 ± 0.0052
<i>m</i> -NO <sub>2</sub>	0.0191 ± 0.0014

<sup>a</sup> See footnote a in Table I.

Excluding the rates for the methoxy compounds, which appear to be abnormally high, the logarithms of these relative rate constants were plotted against two different sets of  $\sigma$  values<sup>14,15</sup> and two different sets of  $\sigma^+$  values.<sup>16,17</sup> The best Hammett correlation was obtained with the  $\sigma^+$  values of Brown and Okamoto<sup>16</sup> which gave a  $\rho$  value of  $-2.91 \pm 0.29$ .<sup>18</sup> The plot of this correlation is given in Figure 1.

In an attempt to determine whether the oxidative decarboxylation of phenylacetic acids by CAN proceeds through a radical intermediate, the oxidation of *p*-methylphenylacetic acid was carried out in the presence of oxygen. After several experiments, it was found that if the reaction was carried out in the absence of added nitric acid and at 25° in 50% aqueous aceto-

(13) L. B. Young and W. S. Trahanovsky, *J. Amer. Chem. Soc.*, **91**, 5060 (1969).

(14) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

(15) R. W. Taft, *J. Phys. Chem.*, **64**, 1805 (1960).

(16) H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958).

(17) C. G. Swain and E. L. Lupton, *J. Amer. Chem. Soc.*, **90**, 4328 (1968).

(18) The plot using  $\sigma^+$  values of Swain and Lupton<sup>17</sup> gave  $\rho = -2.74 \pm 0.38$ , the one using  $\sigma$  values of Jaffé<sup>14</sup> gave  $\rho = -3.15 \pm 0.38$ , and the one using  $\sigma$  values of Taft<sup>15</sup> gave  $\rho = -3.12 \pm 0.43$ .

**Table III.** Oxidation of *p*-Tolylacetic Acid (400 mmol) with CAN (800 mmol) under Nitrogen and under Oxygen in the Presence and Absence of Benzyl Alcohol

Atmo- sphere	Benzyl alcohol, mmol	Products, mmol				
		<i>p</i> -TolCHO	<i>p</i> -TolCH <sub>2</sub> OH	<i>p</i> -TolCH <sub>2</sub> ONO <sub>2</sub>	PhCHO	PhCH <sub>2</sub> OH
N <sub>2</sub>		0.56	0.88	1.08		
O <sub>2</sub>		1.91	0.28	0.21		
O <sub>2</sub>	1.00	1.51	0.18	0.21	0.56	0.43

nitrile, the products were different if the reaction was carried out under nitrogen or oxygen. In a control experiment, 1.00 mmol of benzyl alcohol was added to the reaction mixture of an oxidation of 4.00 mmol of *p*-methylphenylacetic acid in the presence of oxygen. The results from these oxidations are shown in Table III. In the run containing benzyl alcohol the decrease in the total yield of products from the acid is 0.50 mmol while the yield of benzaldehyde from the benzyl alcohol oxidation is 0.56 mmol.

Another control experiment involved using a cerium (III) (cerium(IV) reduced with pinacol) solution with added *p*-methylbenzyl nitrate. Oxygen was bubbled through the solution for the same period of time as the oxidative decarboxylation of *p*-methylphenylacetic acid. The reaction mixture was worked up identically to the work-up for the oxidative decarboxylations. The analysis of the residue was performed by nmr and showed 0.58 mmol of *p*-methylbenzyl nitrate and 0.30 mmol of *p*-methylbenzyl alcohol from an initial 0.95 mmol of *p*-methylbenzyl nitrate.

In order to establish that the  $\rho$  for the decarboxylation was not significantly different in 30% aqueous acetonitrile containing nitric acid (0.35 *M*) or 50% acetonitrile containing no added nitric acid, some competitive oxidations were carried out in the latter medium. The relative rates of oxidation from these experiments are present in Table IV. The logarithms of

**Table IV.** Relative Rates of CAN Oxidation of Substituted Phenylacetic Acids, ZC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>COOH, in 50% Aqueous Acetonitrile<sup>a</sup>

Z	$k_Z/k_H$
<i>p</i> -CH <sub>3</sub>	20.4 ± 0.5
<i>m</i> -CH <sub>3</sub>	5.97 ± 0.34
H	(1.00)
<i>p</i> -Cl	1.12 ± 0.05
<i>m</i> -Cl	0.177 ± 0.004

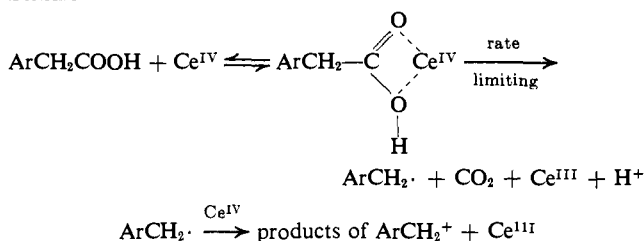
<sup>a</sup> With no added nitric acid at 80°. <sup>b</sup> Standard deviations based on at least three runs.

the rate constants plotted against  $\sigma^+$  values given by Brown and Okamoto<sup>16</sup> gave a  $\rho$  value of  $-2.93 \pm 0.48$ .

Confirmation that the relative rates were the same in the presence of oxygen or nitrogen was gained by measuring the relative rate of oxidation of *p*-methylphenylacetic acid *vs.* phenylacetic acid in 50% aqueous acetonitrile at 25° in the presence of oxygen. Three runs gave  $k_{p\text{-CH}_3}/k_H = 20.0 \pm 1.8$ .

### Discussion

The results of the present study support the mechanism given in Scheme I for the cerium(IV) oxidative decarboxylation of carboxylic acids. That this mech-

**Scheme I**

anism involves a complex is reasonable since evidence for a complex in the cerium(IV) oxidation of acetic acid has been obtained.<sup>11</sup> The complex is drawn with the carboxyl group as a bidentate ligand since the nitrates around CAN are bidentate ligands in the solid phase<sup>19</sup> and probably also in solution<sup>20</sup> and a carboxyl group is analogous to a nitrate ligand.

Conformation that benzyl radicals are intermediates was obtained from the oxygen-trapping experiments. In the oxidation of *p*-methylphenylacetic acid, the yield of *p*-methylbenzaldehyde increased fourfold while the yield of benzyl nitrate decreased fourfold when oxygen was bubbled through the reaction mixture. The increase in the yield of aldehyde is consistent with the trapping of an intermediate *p*-methylbenzyl radical with oxygen to yield a *p*-methylbenzylperoxy radical which undergoes subsequent decomposition.<sup>21</sup> The results of two control experiments indicate that the increase in the yield of aldehydes and the decrease in the yield of benzyl nitrate are not a result of the presence of oxygen alone. In the oxidation of *p*-methylphenylacetic acid with added benzyl alcohol, product analysis indicated that the benzaldehyde:benzyl alcohol ratio was 56:43 while the *p*-methylbenzaldehyde:*p*-methylbenzyl alcohol ratio was 151:18. This large difference in ratios indicates that the two different aldehydes are generated by two different processes. The reaction of *p*-methylbenzyl nitrate with cerium(III) and oxygen showed that only *p*-methylbenzyl nitrate and *p*-methylbenzyl alcohol were components of the reaction mixture. No evidence for *p*-methylbenzaldehyde could be found. Presumably, *p*-methylbenzyl alcohol results from the hydrolysis of *p*-methylbenzyl nitrate.

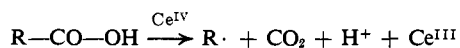
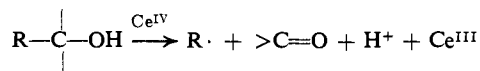
The competitive oxidation of *p*-methylphenylacetic acid *vs.* phenylacetic acid by CAN under an oxygen atmosphere indicates that oxygen has no effect on the relative rates of oxidation of the two acids. These results suggest that the same mechanism of decarboxylation operates in the presence or absence of oxygen.

The formation of the radical is in agreement with Sheldon and Kochi's work<sup>10</sup> and is expected considering the analogy between oxidative decarboxylation and oxidative cleavage of alcohols, a one-electron pro-

(19) T. A. Beineke and J. Delgaudio, *Inorg. Chem.*, **7**, 715 (1968).

(20) R. D. Larsen and G. H. Brown, *J. Phys. Chem.*, **68**, 3060 (1964).

(21) G. A. Russell, *J. Amer. Chem. Soc.*, **79**, 3871 (1957).



cess which has been shown to be readily brought about by cerium(IV).<sup>22</sup>

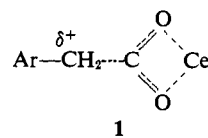
The conversion of the radical to the final products has been discussed previously.<sup>10, 22e</sup> The products observed are the same ones that have been observed from other CAN oxidations that involve benzyl radicals.<sup>18, 22, b, d</sup>

The relative rates of oxidation of substituted phenylacetic acids given in Table II clearly indicate that there is a pronounced substituent effect on the rate of decarboxylation. Excluding the data for the methoxy acids,  $\rho$  values of *ca.*  $-3$  were obtained from correlations of these relative rates with various series of  $\sigma$  values with the best correlation giving a value of  $-2.91 \pm 0.29$ . The fact that the best correlation was obtained with  $\sigma^+$  values is not too surprising since the rate data for many reactions that involve benzyl radicals correlates better with  $\sigma^+$  values than  $\sigma$  values.<sup>23</sup> However, the large negative value of the  $\rho$  for the decarboxylation is unusual since  $\rho$  values for most processes leading to a benzyl radical in the rate-determining step are in the range of  $-0.3$  to  $-1.5$ . The  $\rho$  values for processes leading to benzyl cations in the rate-determining step are usually in the range of  $-3.5$  to  $-6.5$ <sup>14, 16, 24</sup> and thus, the value for the oxidative decarboxylation of substituted phenylacetic acids by CAN falls between these two  $\rho$  value ranges. However, a  $\rho$  of  $-2.00$  was obtained for the oxidative cleavage of 2-aryl-1-phenylethanols by CAN,<sup>22b, d</sup> an oxidation which is a one-electron process that produces benzyl radicals in the rate-determining step.

The large negative  $\rho$  value and the better correlation with  $\sigma^+$  values for the CAN oxidative decarboxylation of phenylacetic acids suggests that a fairly large amount of positive charge develops on the benzylic carbon atom during the cleavage step. Evidently the cerium atom is able to polarize the transition state of the reaction which forms the benzyl radical more than the transition states of previously reported reactions that form benzyl radicals which, in fact, do not involve metal ions.<sup>23</sup>

The large negative  $\rho$  value for the oxidative decarboxylation of phenylacetic acids by CAN eliminates the formation of either a carboxyl radical or a carboxyl

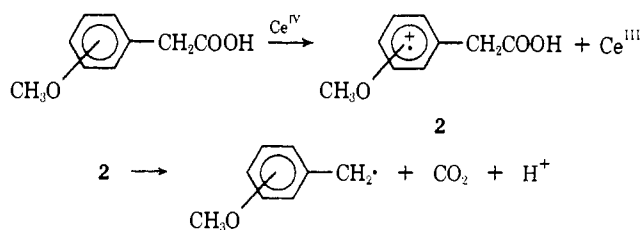
cation as the rate-determining step since the substituent effect for either of these processes should be small as indicated by the small change in  $pK_a$  values for the substituted phenylacetic acids.<sup>12</sup> We believe that structure **1** is a good representation of the transition state for



the rate-determining step of the CAN oxidative cleavage of phenylacetic acids.

The large negative  $\rho$  value which we have observed for the CAN oxidation of phenylacetic acids suggests that carboxylic acids which can lead to the formation of a group which is a stable cation should be relatively easily decarboxylated by CAN. Thus, acids which can lead to tertiary alkyl radicals should be more rapidly decarboxylated than those which lead to secondary or primary alkyl radicals, a prediction which gets some support from the data of Sheldon and Kochi.<sup>10</sup> Also, the rapid decarboxylation of 2,4,6-cycloheptatriene-carboxylic acid by CAN to give the tropylium ion supports this idea.<sup>25</sup>

The unusually rapid rates of oxidation of both *m*- and *p*-methoxyphenylacetic acid suggest that these acids are oxidized *via* a different mechanism than acids which contain a less electron-rich phenyl ring. Quite probably these oxidations involve the initial formation of the radical cation of the aromatic ring.<sup>26</sup>



## Experimental Section

**Methods and Materials.** Most equipment and methods have been previously described.<sup>18</sup> The CAN was obtained from Baker Chemical Co., phenylacetic and *p*-nitrophenylacetic acids were obtained from Eastman Organic Chemicals, and *p*-fluorophenylacetic acid was obtained from Pierce Chemical Co. *p*-Bromo-, *m*-chloro-, *p*-chloro-, *m*-methoxy-, *p*-methoxy-, and *p*-methylphenylacetic acids were obtained from Aldrich Chemical Co., Inc. The *p*-bromo-, *p*-chloro-, *m*-methoxy-, and *p*-methoxy acids were recrystallized from carbon tetrachloride. The *p*-methyl acid was recrystallized from hexane or heptane.

*m*-Nitrophenylacetic acid was prepared by converting *m*-nitrobenzyl alcohol (Aldrich) to the chloride<sup>27</sup> and then to the acid *via* the nitrile;<sup>28</sup> mp 117–118° (lit.<sup>29</sup> mp 117°); nmr (DMSO-*d*<sub>6</sub>)  $\delta$  11.5 (broad s, 1), 8.2–7.4 (m, 4), and 3.79 (s, 2).

*m*-Methylphenylacetic acid was prepared from the benzyl alcohol (Aldrich) by the procedure used for the *m*-nitro acid: mp 61–62° (lit.<sup>30</sup> mp 61°); nmr (CDCl<sub>3</sub>)  $\delta$  11.5 (s, 1), 7.06 (m, 4), 3.52 (s, 2), and 2.28 (s, 3).

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*p*-Methylbenzyl nitrate was prepared by the procedure of Ferris, *et al.*:<sup>31</sup> bp 70–72° (0.5 mm) (lit.<sup>32</sup> bp 60° (0.2 mm)); nmr (CCl<sub>4</sub>) $\delta$  7.15 (s, 5), 5.27 (s, 2), and 2.33 (s, 3).

**Competitive Oxidations.** All competitive oxidations were carried out in a similar fashion but two different work-up procedures were employed. In order to make the nmr determination as accurate as possible, runs involving acids with methyl groups were worked up by a method which separated the recovered phenylacetic acids from the neutral reaction products.

**General Procedure A.** To 2.00 mmol of each of the appropriate phenylacetic acids in 40 ml of 30% aqueous acetonitrile containing nitric acid (0.35 *M*) was added 10 ml of a CAN solution in the same solvent (amounts of CAN varied depending on the substrates). The reaction mixture was heated on a steam bath with stirring until the mixture had decolorized. The mixture was cooled, standard (1.00 mmol of bibenzyl or 1.33 mmol of 2,4-dinitrotoluene) was added, and the mixture was poured into 25 ml of saturated aqueous sodium chloride (saturated NaCl) solution. The mixture was extracted three times with 25-ml portions of ether and combined ether extracts were washed one time with 25 ml of saturated NaCl solution, dried (MgSO<sub>4</sub>), and concentrated on a rotary evaporator. The residue was dissolved in CDCl<sub>3</sub> and analyzed by nmr.

**General Procedure B.** The reaction was carried out as described in procedure A and after the reaction mixture was cooled, standard (2.00 mol of *o*-toluic acid) was added and the mixture was poured into 25 ml of saturated NaCl solution. The mixture was extracted three times with 25-ml portions of ether and combined ether extracts were washed two times with 10-ml portions of 1.2 *M* aqueous sodium hydroxide solution. The resulting alkaline solution was acidified with 5 ml of 6.0 *M* nitric acid and extracted three times with 10-ml portions of ether. These last ether extracts were combined, dried (MgSO<sub>4</sub>), and concentrated. The residue was dissolved in CDCl<sub>3</sub> and analyzed by nmr.

**Nmr Analysis.** Spectra were taken on the 250-Hz scale and the pertinent peaks were integrated several times. The relative areas of the various peaks to that of the standard peaks were corrected by multiplying by extraction ratios (which ranged from 0.936 to 1.023) which were determined by using pre-reduced CAN solutions. In procedure A, the ratios of the recovered starting materials were determined from expanded (50 Hz) peaks of the methylene protons which were cut out and weighed. In procedure B, the ratios of the recovered starting materials were obtained by multiplying the area of the peaks for the methylene protons by 1.5 and subtracting from this value the area of the peak for the methyl group of one of the acids. All determinations were based on several runs and multiple integrations.

**Radical trapping experiments** were performed under nitrogen or oxygen in a 100-ml, three-necked round-bottomed flask equipped with a sintered glass bubbler, reflux condenser, and addition funnel with a pressure equalizing side arm. The system was flushed with nitrogen or oxygen for 5 min prior to the start of the reaction and for nitrogen a positive pressure was maintained throughout the reaction while the oxygen was bubbled through the mixture throughout the reaction. Into the flask was placed 4.00 mmol of *p*-methylphenylacetic acid in 35 ml of 50% aqueous acetonitrile followed by

15 ml of a 50% aqueous acetonitrile solution of 8.00 mmol of CAN. The reaction mixture was magnetically stirred at 25  $\pm$  2° until the solution was decolorized. Standard (1.00 mmol of mesitylene) was added and the mixture was poured into 25 ml of saturated NaCl solution. The mixture was extracted three times with 25-ml portions of ether and the combined ether extracts were washed three times with 10-ml portions of 1.2 *M* aqueous sodium hydroxide solution and three times with 25-ml portions of saturated NaCl solution. The ether solution was dried (MgSO<sub>4</sub>) and concentrated. The residue taken was dissolved in CDCl<sub>3</sub> and analyzed by nmr.

**Competitive Oxidations under Oxygen.** To 2.00 mmol each of *p*-methylphenylacetic acid and phenylacetic acid in 35 ml of 50% aqueous acetonitrile which had been flushed for 5 min with oxygen, was added 4.00 g of CAN in 15 ml of 50% aqueous acetonitrile. The reaction mixture was stirred mechanically at room temperature until the mixture had decolorized, during which time oxygen was bubbled through the reaction mixture. Standard (2.00 mmol of *o*-toluic acid) was added and the mixture was poured into 25 ml of saturated NaCl solution and extracted three times with 25-ml portions of ether. The combined ether layers were washed two times with 10 ml of 1.2 *M* aqueous sodium hydroxide solution. The alkaline solution was acidified with 5 ml of 6.0 *M* aqueous nitric acid and the resulting mixture was extracted three times with 10 ml of ether. The ether solution was dried (MgSO<sub>4</sub>) and concentrated. The residue was dissolved in CDCl<sub>3</sub> and analyzed by nmr.

**Carbon Dioxide Analysis.** Nitrogen was bubbled through 40 ml of 70% aqueous acetonitrile containing nitric acid (0.35 *M*) and 4.00 mmol of *p*-methylphenylacetic acid and then through three U-tubes with the first one containing anhydrous calcium chloride, the second one containing Ascarite, and the third one containing anhydrous calcium chloride and then through a gas bubbler for several minutes. A solution of 8.8 mmol of CAN in 10 ml of the same solvent which had previously been degassed was added and the reaction mixture was heated at 55° with nitrogen bubbling until the mixture had decolorized. The nitrogen bubbling was continued for another 5 min, the absorption train broken, and the U-tube containing the Ascarite immediately weighed. The amount of carbon dioxide adsorbed was determined by the weight difference of the Ascarite U-tube before and after the reaction.

**Control Reaction with Added Benzyl Alcohol.** To 4.00 mmol of *p*-methylphenylacetic acid and 1.00 mmol of benzyl alcohol in 40 ml of 50% aqueous acetonitrile was added 8.00 mmol of CAN in 10 ml of 50% aqueous acetonitrile. The reaction was run at room temperature with oxygen bubbling through the reaction mixture until the solution had decolorized. Standard was added and the mixture was worked up as previously described and analyzed by nmr.

**Control Reaction with *p*-Methylbenzyl Nitrate.** To 50 ml of a 50% aqueous acetonitrile solution of cerium(III) (prepared by reducing CAN with pinacol) was added 0.95 mmol of *p*-methylbenzyl nitrate. Oxygen was bubbled through the reaction mixture for the same length of time as the decarboxylation at room temperature. The mixture was worked up as previously described and shown to contain 0.58 mmol of *p*-methylbenzyl nitrate and 0.30 mmol of *p*-methylbenzyl alcohol by nmr analysis.

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