by subtracting the spectrum of **6a** from the spectrum of this mixture.

Acknowledgment. The technical assistance of Barbara Jean Dias and Ashoke Sinha was appreciated.

Registry No. **1a**, 54047-80-1; **1b**, 21059-36-9; **1c**, 72049-90-2; **1d**, 72049-91-3; **1e**, 2342-71-4; **1f**, 1448-36-8; **1g**, 33744-75-1; **1h**, 6818-44-6; **1i**, 55106-11-1; **1j**, 72049-92-4; **1k**, 64219-21-2; **2a**, 72059-84-8; **2b**, 72049-93-5; **3a**, 72049-94-6; **3b**, 72049-95-7; **3c**, 72049-96-8; **3d**, 72049-97-9; **4**, 72049-98-0; **5a**, 601-95-6; **5b**, 72049-99-1; **5c**, 72050-00-1; **5d**, 72050-01-2; **5e**, 61543-88-2; **5f**, 69889-99-2; **5g**, 69890-00-2; **6a**, 72050-02-3; **6b**, 72050-03-4; **6c**, 72050-04-5.

Notes

Electron-Transfer Processes: Oxidation of 4-Phenylbutanoic Acid by Cobaltic Acetate

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The oxidative decarboxylation of arylacetic acids by cobalt(III) acetate in the presence of copper(II) acetate in acetic acid has been ascribed to the formation of an aromatic radical cation intermediate.[1]

The high value of ρ (−2.9) for the decarboxylation of substituted arylacetic acids and the exclusive formation of 4-phenylbutyrolactone in the cobaltic oxidation of 4-phenylbutanoic acid has been reported as evidence for the proposed mechanism.

In this note, we describe our results on oxidation of 4-phenylbutanoic acid by cobalt(III) acetate under various experimental conditions, which include also those previously reported,[1] and by cobalt(III) acetate in the presence of copper(II) acetate, respectively. In all cases, the oxidative decarboxylation of **1** (path A) competes with the formation of **2** (path B) (Scheme I). The 3-phenylpropyl radical reacts by hydrogen abstraction, giving 1-phenylpropane (**3**) in the absence of Cu(II) salts, while in the presence of Cu(II) salts the olefins **4** ($PhCH_2CH{=}CH_2$) and **5** ($PhCH{=}CHCH_2OAc$) are formed.

$$PhCH_2CH_2CH_2\cdot + Cu^{2+} \rightarrow \underset{\mathbf{4}}{PhCH_2CH{=}CH_2} + Cu^+ + H^+$$

Compound **5** comes from further oxidation of **4**.

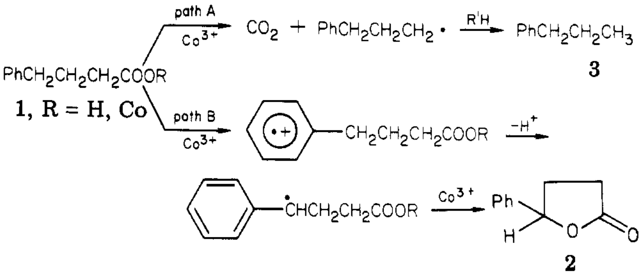
$$PhCH_2CH{=}CH_2 \xrightarrow[-Co^{2+},\ -H^+]{Co^{3+}} Ph\dot{C}HCH{=}CH_2 \rightarrow PhCH{=}CHCH_2\cdot$$

$$PhCH{=}CHCH_2\cdot + Co(OAc)_3 \rightarrow \underset{\mathbf{5}}{PhCH{=}CHCH_2OAc} + Co(OAc)_2$$

Competitive oxidation of acetic acid by Co(III) is also responsible for the observed low conversion of **1**.

Our results are not in favor of a single mechanism[1] and suggest that a dualism of mechanism (electron transfer from the aromatic ring and from the anion carboxylate) is operating in the oxidation of arylacetic acids and of 4-phenylbutanoic acid by Co(III) salts.[2]

Scheme I



A similar mechanism has already been suggested for the oxidation of phenylacetic acid by Ce(IV) salts;[3] this conclusion was criticized on the basis of the results obtained by Co(III) salts.[1]

Very similar results were obtained also in the oxidation of 4-phenylbutanoic acid with peroxydisulfate, indicating that an analogous dualism of mechanism is operating also in that case.

Experimental Section

Potassium peroxydisulfate and copper(II) acetate monohydrate were obtained from Fluka and Carlo Erba, respectively. 4-Phenylbutanoic acid, 3-phenylpropane, and 3-phenylpropene were commercial products (Fluka). The olefin **5** was prepared by $NaBH_4$ reduction of cinnamaldehyde and esterification with acetic anhydride and pyridine of the resulting alcohol. The lactone **2** was identified by comparison with the authentic sample.[4] The 4-phenyl-4-acetoxybutanoic acid was prepared starting with 4-phenyl-4-hydroxybutanoic acid and esterification with acetic anhydride and pyridine. Cobalt(III) acetate was prepared (>97% purity) according to the reported procedure.[5]

All solvents and reagents were checked for purity and found to be free from the products **1**, **2**, **3**, **4**, and **5**.

All experiments were carried out under N_2.

Cobaltic Oxidation of 4-Phenylbutanoic Acid. (a) In the Absence of $Cu(OAc)_2$. A solution of 5.7 g (0.035 mol) of 4-phenylbutanoic acid in a 0.66 M $Co(OAc)_3$ acetic acid solution (50 mL) was heated at reflux for 2 h. The solution was poured into water, acidified with HCl, and extracted by ether (2 × 50 mL). On the combined extracts an acid–base separation was carried out with a saturated solution of Na_2CO_3 and 10% HCl. The neutral fraction, after addition of methyl benzoate as the internal standard, was analyzed by GLC on a glass column (2 m) of 10% UCC W 982 on Chromosorb P (80–100 mesh) with a GLC "Hewlett Packard" Model 575. The yields of the lactone **2** and

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[1] R. M. Dessau and E. I. Heiba, *J. Org. Chem.*, **40**, 3647 (1975).

[2] It was suggested by a referee that the detection of oxidative cleavage via the free-radical route from **1** path A indicated that this would be the exclusive pathway for phenylacetic acid oxidation.

[3] W. S. Trahanovsky, J. Cramer, and D. W. Brixin, *J. Am. Chem. Soc.*, **96**, 1077 (1974).

[4] A. Clerici, F. Minisci, and O. Porta, *Tetrahedron Lett.*, 4183 (1974).

[5] S. S. Lande, J. D. Salk, and J. K. Kochi, *J. Inorg. Nucl. Chem.*, **33**, 4101 (1971).

0022-3263/80/1945-0345$01.00/0

1-phenylpropane (3), based on converted 4-phenylbutanoic acid, were 35 and 5%, respectively. The nature of the product was determined on the basis of the data of the GLC MS system (Varian Mat 112 S) operating at an ionizing potential of 70 eV and an accelerating potential of 816 V (**3**, C_9H_{12} MS *m/e* 91 (100), 120 (22), 92 (10), 65 (9), 78 (8), 51 (5), 105 (4)). In a parallel experiment, a neutral portion was chromatographed on silica gel (pentane–ethyl ether) and the product **3** was isolated as pure product by preparative GLC from an enriched chromatographic fraction and compared (IR, NMR, MS spectra) with authentic sample. The acid fraction was treated with diazomethane in excess and analyzed by GLC as was done previously. The conversion of 4-phenylbutanoic acid was 27%. The yield of the 4-phenyl-4-acetoxybutanoic acid, based on converted 4-phenylbutanoic acid, was 16%.

(b) In the Presence of $Cu(OAc)_2$. The reaction was carried out as in (a) in the presence of 18 mmol of $Cu(OAc)_2{\cdot}H_2O$. The conversion of 4-phenylbutanoic acid was 31%. The yields of lactone **2**, 4-phenyl-4-acetoxybutanoic acid, and the olefins **4** and **5**, based on converted 4-phenylbutanoic acid, were respectively 34, 8, 9, and 8%. The olefins **4** and **5** were isolated as was done previously by chromatography on silica gel and compared with authentic samples (**4**, C_9H_{10}, MS *m/e* 117 (100), 118 (80), 91 (40), 115 (25), 39 (25), 51 (17), 65 (14), 78 (10)).

Oxidation of 4-Phenylbutanoic Acid by Peroxydisulfate and $Cu(OAc)_2$. A mixture of 4-phenylbutanoic acid (20 mmol), $K_2S_2O_8$ (20 mmol), KOAc (45 mmol), and $Cu(OAc)_2{\cdot}H_2O$ (10 mmol) in 50 mL of acetic acid was refluxed for 2 h. The mixture was then poured into water, separated as was done previously, and analyzed by GLC. The conversion of 4-phenylbutanoic acid was 34%. The yield of the lactone **2**, 4-phenyl-4-acetoxybutanoic acid, and the olefins **4** and **5**, based on converted 4-phenylbutanoic acid, was 40, 3, 15, and 6%, respectively.

Registry No. 1 (R = H), 1821-12-1; **2**, 1008-76-0; **3**, 103-65-1; **4**, 300-57-2; **5**, 103-54-8; 4-phenyl-4-acetoxybutanoic acid, 71948-82-8; $Co(OAc)_3$, 917-69-1; $Cu(OAc)_2$, 142-71-2; $K_2S_2O_8$, 7727-21-1.

Oxidation of 7-(Hydroxymethyl)bicyclo[3.3.1]nonan-3-ol. Convenient Synthesis of Bicyclo[3.3.1]nonane-3,7-dione

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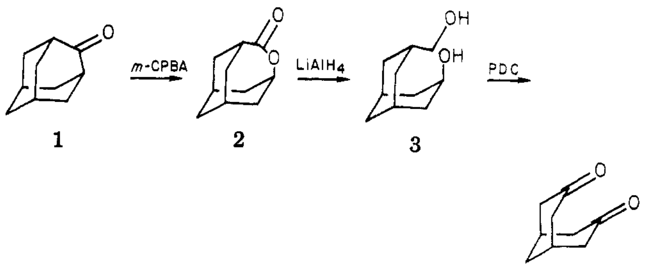
Bicyclo[3.3.*n*]alkane-3,7-diones are important intermediates in synthetic routes to alkenes containing pyramidalized carbon atoms.[1] The *n* = 1 diketone (**4**) can be prepared in three steps, starting from adamantane.[2] However, the second step in the sequence, the transformation of 1,3-dibromoadamantane into 7-methylenebicyclo[3.3.1]nonan-3-one, requires the use of an autoclave. The size of the autoclave available to us severely limited the amount of **4** that we could prepare in one batch; we therefore sought a more convenient route to this diketone.

Peters et al. have found that the oxidation of *endo*-7-alkyl-3-(hydroxymethyl)bicyclo[3.3.1]nonanes gives *endo*-7-alkylbicyclo[3.3.1]nonan-3-ones.[3] Although no explanation for this remarkable transformation was proposed, on the basis of this result it seemed possible that diol **3** could be oxidized directly to the diketone **4**. We report herein the success of this reaction as the key step in a convenient, high-yield, three-step synthesis of **4** from the commercially available 2-adamantanone (**1**) (see Scheme I)

Scheme I



1 2 3

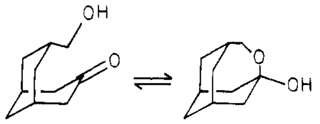
4

Oxidation of **1** with *m*-chloroperbenzoic acid gives the lactone **2**,[4] which can be reduced to the diol **3** with $LiAlH_4$.[5] Although the oxidation proceeds in excellent yield (96%),[4] only a 66% yield has been reported for the reduction.[5] We have found that the diol **3** is only sparingly soluble in ether. Consequently, if hot tetrahydrofuran is used instead of ether to wash the alumina salts formed in the workup of the reduction, **3** can be isolated in nearly quantitative yield from this reaction.

After some experimentation we discovered that pyridinium dichromate (PDC)[6] oxidation of **3** for 18 h in dichloromethane provides essentially pure **4** in 75% yield. Other chromium-based reagents (Jones, Fieser, CrO_3/acetic acid, and pyridinium chlorochromate) also convert **3** to **4**, but with these reagents the diketone **4** is obtained in lower yields and is accompanied by other oxidation products.

The transformation of **3** to **4** represents an apparently rare example of pyridinium dichromate in methylene chloride oxidizing a primary alcohol beyond the aldehyde stage.[6] We use a large excess of oxidizing agent, but under similar reaction conditions benzyl alcohol is only oxidized to benzaldehyde and cyclohexylmethanol to cyclohexanecarboxaldehyde.

The secondary hydroxyl in **3** is oxidized faster than the primary hydroxyl, presumably because of the greater relief of steric interactions on formation of the ketone.[7] When the reaction is terminated after 2 h, the major product is the keto alcohol **5**, obtained as an equilibrium mixture in which the lactol form **6** dominates. Resubmission of this mixture to the reaction conditions for an additional 16 h gives **4**.



5 6

The formation of **4** from **5** is noteworthy, since **5** lacks the endo substituent that Peters found necessary for ox-

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[1] R. Greenhouse, W. T. Borden, K. Hirotsu, and J. Clardy, *J. Am. Chem. Soc.*, **99**, 1664 (1977).

[2] A. R. Gagneux and R. Meier, *Tetrahedron Lett.*, 1365 (1969).

[3] J. A. Peters, J. M. VanDer Toorn, and H. Van Bekkum, *Tetrahedron*, 31, 2273 (1975).

[4] This reaction can be done with a number of peroxidizing reagents; see, for example, G. Mehta and P. N. Pandry, *Synthesis*, 404 (1975).

[5] H. Wynberg, A. C. Udding, and J. Strating, *Tetrahedron Lett.*, 5719 (1968). These authors report a 66% yield with no experimental data.

[6] E. J. Corey and G. Schmidt, *Tetrahedron Lett.*, 399 (1979).

[7] H. House, "Modern Synthetic Reactions", 2nd ed., W. A. Benjamin, Menlo Park, CA, 1972, p 261.

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