

1.8), C-2)], 11 [s, 2 (\*NH, OH)].

Anal. Calcd for  $C_7H_9F_3N_2O_3$ : C, 37.18; H, 4.01. Found: C, 37.39; H, 4.04.

**Reaction of 2 with Hydrochloric Acid and Reduction of 4b to 5.** An excess of dry hydrogen chloride gas was bubbled through a solution of 1.1 g (10 mmol) of 1-nitroso-1,2,3,4-tetrahydropyridine (2) in 30 mL of chloroform at 0 °C. The solid that formed was collected by filtration to give 0.7 g (4.8 mmol) (48%) of 3-oximino-3,4,5,6-tetrahydropyridinium chloride (4b); mp 155–159 °C dec. The spectral properties were nearly identical with those of 4a.

The rearrangement product 4b (1.15 g, 7.7 mmol) in 40 mL of MeOH was added to an excess of sodium borohydride in 30 mL methanol at 0 °C. After being stirred for 2 h, the reaction mixture was concentrated under reduced pressure. The residue was triturated with acetone, and the acetone solution was treated with anhydrous hydrogen chloride for 5 min. The solid that formed was removed by filtration to give a quantitative yield of solid, which on recrystallization from ethanol gives the 3-piperidone oxime hydrochloride (5), as a mixture of *Z* and *E* isomers: mp 115–145 °C dec; NMR ( $D_2O$ )  $\delta$  [multiplicity, integration (assignment)] 2.4 [m, 2 (C-5)], 3.1 [t, 2 (C-4)], 3.8 [t, (C-6)], 4.1 and 4.4 [s, 2 (C-2 in *Z* and *E* isomer)]. (The signal at  $\delta$  4.4 is only 33% of that at 4.1.)

Anal. Calcd for  $C_5H_{11}ClN_2O$ : C, 39.88; H, 7.34. Found: C, 39.85; H, 7.36.

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**Registry No.** 2, 70501-82-5; 4a, 86834-59-5; 4b, 86834-60-8; (*Z*)-5-HCl, 86834-61-9; (*E*)-5-HCl, 86834-62-0; trifluoroacetic acid, 76-05-1; hydrogen chloride, 7647-01-0.

### Persulfate/Silver Ion Decarboxylation of Carboxylic Acids. Preparation of Alkanes, Alkenes, and Alcohols

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The persulfate ion,  $S_2O_8^{2-}$ , is an inexpensive and easily handled oxidant that has seen little use in synthetic organic chemistry.<sup>1</sup> Its high reduction potential ( $E^\circ = 2.01$  V, aqueous) makes persulfate a powerful oxidant; however, the high activation barrier (approximately 30 kcal/mol) to uncatalyzed homolytic decomposition renders persulfate less useful at reasonable temperatures. The actual reactive species, sulfate radical anion,  $SO_4^{\cdot-}$ , is also not very efficient at oxidizing many organic functional groups. Transition-metal catalysts greatly facilitate the decomposition of persulfate. They allow reactions at lower temperatures as well as produce higher oxidation state metal ions that are capable of performing unique oxidations themselves.

The persulfate/silver ion combination has been most widely used, and in particular, Anderson and Kochi have investigated the mechanism of carboxylic acid decarboxylation by this reagent pair.<sup>2</sup> Their work identified many

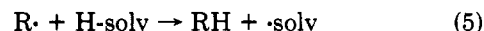
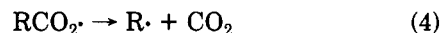
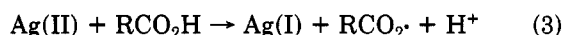
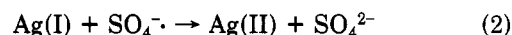
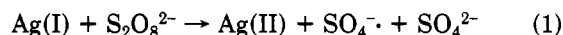
of the mechanistic features of the decarboxylation of carboxylic acids with the persulfate/silver system; however, they consistently used a vast excess of carboxylic acid in the kinetic experiments. Thus the synthetic potential was not demonstrated. Other workers have used this same reagent pair to produce organic radicals for other purposes.<sup>3</sup> In this note we describe our results, which show that silver(II)-catalyzed decarboxylation is a synthetically useful reaction for producing alkanes, alkenes, or alcohols. Our choice of experimental conditions also gives either exclusively one product or a much simpler product mixture than observed previously.<sup>2</sup> Other decarboxylation methods such as *tert*-butyl perester decomposition,<sup>4</sup> copper/quinoline,<sup>5</sup> or lead tetraacetate<sup>6</sup> all have drawbacks such as the high temperature required or myriad of products produced. While our present method is not without flaw (*vide infra*) it is simple, fast (20-min reaction time), and proceeds predictably at moderate temperature (76 °C). The yields are modest, but still compare favorably with other known methods of decarboxylation.

### Results and Discussion

Our silver(II) decarboxylations can be broken down into two types: (1) decarboxylation in a water/acetonitrile solvent combination which led to alkanes by hydrogen abstraction and (2) decarboxylation in the presence of a copper(II) cocatalyst which led to products from the corresponding carbonium ion. The hydrogen abstraction results are presented in Table I and were the result of the slow addition of 2 mol of sodium persulfate to 1 mol of the carboxylic acid and 2 mol % silver nitrate in refluxing 50% aqueous acetonitrile. Total reaction time required was 20 min. An excess of persulfate was found to be necessary to drive the reaction to even 50% completion. The excess persulfate is presumably consumed by oxidation of water.<sup>1</sup> Other water-miscible solvents capable of donating a hydrogen atom (THF, glyme, dioxane) were found to be unsuitable for this reaction as well as several two-phased systems. Table I also includes three entries that employed a stoichiometric amount of silver nitrate; however, this resulted in no substantial improvement over the catalytic silver reaction. By varying the percent of silver catalyst, we demonstrated that the catalyst could be satisfactorily reduced to a 2 mol % level.

The previously proposed mechanism (Scheme I) was

#### Scheme I



found to be consistent with all of our present results.<sup>2</sup> The reactivity of various carboxylic acids, as shown by the extent of conversion, roughly followed the expected order of radical stability ( $3^\circ > 2^\circ > 1^\circ$ ), although the difference in reactivity is small. Unreacted starting material exclusively constituted the acidic material recovered from the

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Table I. Silver(I)/Persulfate Results

entry	acid (RCOOH)	product (RH)	catalytic		stoichiometric	
			conversion, <sup>a</sup> %	yield, <sup>b</sup> %	conversion, <sup>a</sup> %	yield, <sup>b</sup> %
1	nonanoic	octane	44	42	87	48
2	2-ethylhexanoic	heptane	37	65		
3	cyclohexanecarboxylic	cyclohexane	66	52		
4	2-endo-norbornanecarboxylic	norbornane	49	64		
5	1-methylcyclohexanecarboxylic	methylcyclohexane	88	40	85	36
6	1-adamantanecarboxylic	adamantane	69	66 <sup>c</sup>	92	46 <sup>d</sup>
7	2-(phenylmethyl)-2-methylbutanoic	1-phenyl-2-methylbutane	55	55		

<sup>a</sup> Based on recovered starting carboxylic acid. <sup>b</sup> Yield based on GC integration with internal standard. <sup>c</sup> Adamantyl methyl ketone was also obtained in 23% yield. <sup>d</sup> Adamantyl methyl ketone was also obtained in 18% yield.

Table II. Silver(I)- and Copper(II)/Persulfate Results

entry	acid (RCOOH)	convn, <sup>a</sup> %	product (yield, <sup>b</sup> %)
2	2-ethylhexanoic	73	heptenes (58), <sup>c</sup> 3-heptanol (12)
3	cyclohexanecarboxylic	51	cyclohexene (36)
4	1-methylcyclohexanecarboxylic	57	1-methylcyclohexanol (80)
5	1-adamantanecarboxylic	45	1-adamantanol (73)
6	phenylacetic	65	benzaldehyde (63)
7	diphenylacetic	86	benzhydrol (10), benzophenone (62), 1,1,2,2-tetraphenylethane (12)
8	2-phenylbutanoic	73	1-phenyl-1-propanol (73), propiophenone (23), benzaldehyde (4)

<sup>a</sup> Based on recovered starting carboxylic acid. <sup>b</sup> Yield based on GC integration with internal standard. <sup>c</sup> Mixture of 2- and 3-heptenes.

reaction. This was proven by diazomethane esterification and GC analysis. In all cases, except 1-adamantanecarboxylic acid (entry 6), the decarboxylation was clean and the corresponding alkane was the most volatile product. In the case of 1-adamantanecarboxylic acid, hydrogen abstraction was still the major reaction pathway; however, a lesser amount of nucleophilic radical addition to acetonitrile was observed, which produced 1-adamantyl methyl ketone upon hydrolysis within the reaction mixture. Only trace amounts of methyl ketone products were observed for the other acids used. The tendency of tertiary radicals to add in a nucleophilic fashion to acetonitrile has not been previously reported but is entirely consistent with other examples of nucleophilic radical addition to electron-deficient systems.<sup>7</sup>

When the decarboxylation was carried out in the presence of 10 mol % cupric sulfate, the alkyl radical produced in eq 4 was intercepted by copper(II) ion and oxidized via an alkylcopper(II) species.<sup>2,8</sup> The resulting copper(I) was presumably reoxidized by persulfate,<sup>1</sup> since less than equivalent amounts totally change the type of organic products produced. These results are summarized in Table II. In the case of primary radicals, this gave exclusively the alkene by copper oxidation and proton loss. Secondary radicals (entries 2 and 3) led to alkenes and alcohols, while tertiary radicals led exclusively to alcohols. This behavior of 1°, 2°, and 3° alkylcopper(II) species produced by copper(II) sulfate oxidation of the corresponding radical was generally consistent with previous work,<sup>9</sup> although the present degree of specificity is somewhat different than that observed in other solvent systems.<sup>2</sup> Benzyl radicals, produced in entries 6–8, led to a mixture of products that included overoxidation and in entry 7, diphenyl acetic acid,

a small amount (12%) of dimeric coupling product.<sup>10</sup> Experimentally, this silver decarboxylation/copper oxidation could be performed in the presence or absence of acetonitrile and no hydrogen abstraction was observed. The inclusion of pyridine, to promote proton loss,<sup>11</sup> was not found to benefit the reaction but, in fact, resulted in lower yields. Nucleophilic radical addition to the pyridine ring was now also observed.<sup>12</sup>

In conclusion, silver(II) decarboxylation of carboxylic acids is a viable alternative for the preparation of alkanes from any carboxylic acid precursor. The preparation of alkenes from primary radicals and alcohols from tertiary radical intermediates should also be routinely possible. Particular advantages are the low cost of the persulfate oxidant, catalytic use of a silver(I) salt, and moderate temperature. The main drawback is the reactivity of persulfate (catalyzed or thermal) with other organic functionality such as glycols,<sup>13</sup> amines,<sup>14</sup> and olefins.<sup>15</sup> The alkenes produced by this silver(II)/copper(II) method appear to be adequately protected from further oxidation by their low solubility in the aqueous medium employed.

### Experimental Section

Melting points were determined with an Electrothermal apparatus and are uncorrected. <sup>1</sup>H NMR spectra were obtained on a Varian HFT-80 instrument. Chemical shifts are reported in parts per million relative to internal tetramethylsilane. Mass spectra were obtained with an AE1 Ms-30 (electron impact, 70 eV) or a Finnigan 4000 (chemical ionization) spectrometer.

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Gas chromatographic results were obtained with a Varian 3700 instrument equipped with either a 5% Carbowax 20 M on Chromosorb W ( $1/8$  in.  $\times$  2 m) or a 5% SF-96 on Chromosorb W ( $1/8$  in.  $\times$  2 m) column. All products were isolated by preparative GC and gave satisfactory comparison with literature data or authentic samples (NMR, IR, MS, GC retention time).

**General Procedure for Alkane Formation.** The acid or sodium acid salt (1.3 mmol) and silver nitrate (0.025 mmol) were dissolved in acetonitrile (15 mL) and water (5 mL) and heated to reflux. To this solution was added a solution of sodium persulfate (2.6 mmol) in water (10 mL) over 15 min. Refluxing was continued another 5 min before the reaction mixture was cooled and extracted with ether ( $3 \times 10$  mL). The combined ether layers were extracted with a saturated sodium bicarbonate solution ( $3 \times 10$  mL), dried ( $\text{MgSO}_4$ ), and analyzed by GC. Unreacted acid was recovered by acidification of the bicarbonate extractions.

**General Procedure for Alkene/Alcohol Formation.** The acid or sodium acid salt (1.3 mmol), silver nitrate (0.025 mmol), and cupric sulfate (0.13 mmol) were heated to reflux in water (8 mL), and sulfuric acid was added until all copper carboxylate salts dissolved. To this solution was added sodium persulfate (2.6 mmol) in water (7 mL) over 15 min. Refluxing was continued another 5 min, before cooling and work up as above.

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**Registry No.** Nonanoic acid, 112-05-0; 2-ethylhexanoic acid, 149-57-5; cyclohexanecarboxylic acid, 98-89-5; 2-*endo*-norbornanecarboxylic acid, 934-28-1; 1-methylcyclohexanecarboxylic acid, 1123-25-7; 1-adamantanecarboxylic acid, 828-51-3; 2-(phenylmethyl)-2-methylbutanoic acid, 57144-65-7; phenylacetic acid, 103-82-2; diphenylacetic acid, 117-34-0; 2-phenylbutanoic acid, 90-27-7; octane, 111-65-9; heptane, 142-82-5; cyclohexane, 110-82-7; norbornane, 279-23-2; methylcyclohexane, 108-87-2; adamantane, 281-23-2; 1-phenyl-2-methylbutane, 3968-85-2; 1-octene, 111-66-0; 2-heptene, 592-77-8; 3-heptanol, 589-82-2; cyclohexene, 110-83-8; 1-methylcyclohexanol, 590-67-0; 1-adamantanol, 768-95-6; benzaldehyde, 100-52-7; benzhydrol, 91-01-0; benzopenone, 119-61-9; 1,1,2,2-tetraphenylethane, 632-50-8; 1-phenyl-1-propanol, 93-54-9; propiophenone, 93-55-0; silver nitrate, 7761-88-8; sodium persulfate, 7775-27-1; 3-heptene, 592-78-9.

## Synthesis of 10-(Chloromethyl)benzo[*a*]pyrene

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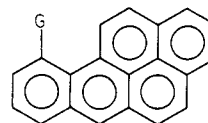
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Received January 24, 1983

As part of a study of the reactions of electrophiles derived from methylbenzo[*a*]pyrenes with nucleophiles related to biological systems, 6-(chloromethyl)benzo[*a*]pyrene<sup>1</sup> and 1-(chloromethyl)benzo[*a*]pyrene<sup>2</sup> have been synthesized and studied.<sup>2,3</sup> These chloromethyl derivatives are readily converted to stabilized arylmethyl cations under solvolytic conditions.<sup>2,3</sup> Studies involving the arylmethyl cation generated from 6-(chloromethyl)benzo[*a*]pyrene have shown that this cation could be trapped readily by nucleosides, deoxynucleosides, and nucleotides

containing adenine, guanine, or cytosine.<sup>4,5</sup>

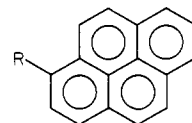
A logical compound for further studies is 10-(chloromethyl)benzo[*a*]pyrene (**1a**), which on solvolysis would



- 1a, G =  $\text{CH}_2\text{Cl}$   
 b, G =  $\text{CH}_2^+$   
 c, G =  $\text{COOEt}$   
 d, G =  $\text{CH}_2\text{OH}$   
 e, G =  $\text{COOMe}$

generate the carbonium ion **1b** with the electrophilic site in the bay region,<sup>6</sup> and we report its synthesis here.

Ethyl 1-pyreneacetate (**2d**) was readily available via the Willgerodt reaction<sup>7</sup> or the Kindler modification thereof<sup>8</sup> on 1-acetylpyrene (**2a**).<sup>7</sup> The Kindler-Willgerodt method



- 2a, R =  $\text{C}(=\text{O})\text{CH}_3$   
 b, R =  $\text{CH}_2$  (with a morpholine ring attached to the bay region)  
 c, R =  $\text{CH}_2\text{COOH}$   
 d, R =  $\text{CH}_2\text{COOEt}$   
 e, R =  $\text{CH}(\text{COOEt})\text{CH}_2\text{CH}_2\text{COOEt}$   
 f, R =  $\text{CH}(\text{COOEt})\text{CH}_2\text{CH}_2\text{COOH}$

was more convenient to carry out and afforded the thiomorpholide **2b** in over 96% yield. Hydrolysis to the acid **2c**<sup>7</sup> followed by conventional esterification afforded **2d** in 70% overall yield.<sup>9</sup>

Treatment of the ester **2d** with ethyl acrylate<sup>10</sup> in the presence of sodium ethoxide gave a 75% yield of the ester **2e**, which was readily converted to the half-ester **2f** by partial hydrolysis (74% yield). Cyclization of **2f** by treatment with anhydrous HF afforded the keto ester **3a** in 71% yield. Reduction of the ester **3a** by the Clemmensen method<sup>11</sup> gave the ester **3c** (87% yield), which was dehydrogenated with DDQ to **1c** in 65% yield. Reduction of the ester **1c** to **1d** was accomplished with lithium aluminum hydride in 96% yield, and **1d** afforded **1a** in 71% yield by treatment with thionyl chloride.

Other approaches to the synthesis of **1a** from the diester **2e** were less satisfactory. One such approach involved a sequence beginning with the keto acid **3b**,<sup>12</sup> and the other

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