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SILVER(I)/PERSULFATE OXIDATIVE DECARBOXYLATION OF CARBOXYLIC ACIDS. ARYLACETIC ACID DIMERIZATION.

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ABSTRACT: The oxidative decarboxylation of arylacetic acids by sodium persulfate and a catalytic amount of silver nitrate produces benzylic radicals which dimerize cleanly to give 1,2-diarylethanes.

The persulfate ion, $S_2O_8^{2-}$, with[1] or without[2] various transition metal catalysts has been previously shown to oxidize both aromatic rings and carboxylic acids.[3] In the course of another study, we have investigated the aqueous silver(I)/persulfate oxidation of several arylacetic acids or their potassium salts. Synthetic and mechanistic aspects of this particular reaction have not been previously investigated, and our results reported here help to better define the catalyzed persulfate oxidation of aryl acids.[4]

Arylacetic acids undergo oxidative decarboxylation by the silver(II) ion which can be produced by persulfate oxidation of silver(I) as shown in Scheme 1. Silver(II) mediated decarboxylation is known to occur with at least a 40 kcal/mol^{-1} lower enthalpy of activation than the corresponding thermal process.[3,5] This decarboxylation mechanism has been

Scheme 1

$$\mathrm{Ag(I)} + \mathrm{S_2O_8}^{2-} \longrightarrow \mathrm{Ag(II)} + \mathrm{SO_4}^{\bar{\cdot}} + \mathrm{SO_4}^{2-}$$

$$\mathrm{Ag(I)} + \mathrm{SO_4}^{\bar{\cdot}} \longrightarrow \mathrm{Ag(II)} + \mathrm{SO_4}^{2-}$$

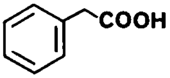
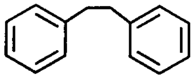
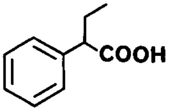
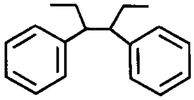
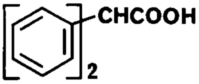
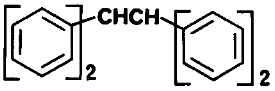
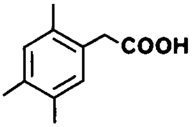
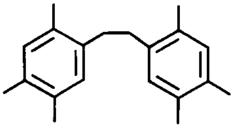
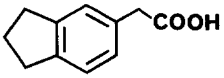
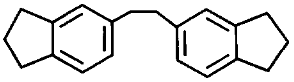
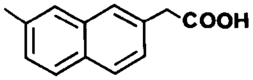
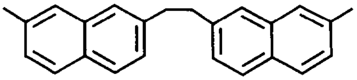
$$\mathrm{Ag(II)} + \mathrm{ArCH_2COOH} \longrightarrow \mathrm{Ag(I)} + \mathrm{ArCH_2CO_2}\cdot + \mathrm{H}^+$$

$$\mathrm{ArCH_2CO_2}\cdot \longrightarrow \mathrm{ArCH_2}\cdot + \mathrm{CO_2}$$

$$2\ \mathrm{ArCH_2}\cdot \longrightarrow \mathrm{ArCH_2CH_2Ar}$$

demonstrated by Kochi *et al.* for aliphatic carboxylic acids. When aliphatic radicals are produced, they may disproportionate, hydrogen-abstract or be further oxidized to an alcohol in aqueous organic media.[3,4] The more stabilized benzylic radical does not effect hydrogen abstraction from either unreacted starting material or solvent, but instead yields the coupled 1,2-diarylethane product as summarized in Table 1.[6,7] No more than trace amounts of hydrogen abstraction or further oxidized products were isolated from the neutral organic fraction. Thus, while the yields are modest, the reaction work-up did not involve a tedious separation, and only 2 mole % of silver nitrate was required and an inexpensive persulfate

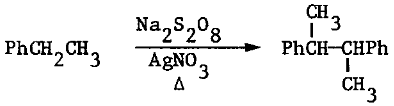
Table 1. Dimerization of Arylacetic Acids

Entry	Acid	Conversion(%)[a]	Product	Yield(%)[b]
1		89		46
2		76		50
3		83		81
4		85		49
5		86		40
6		81		55

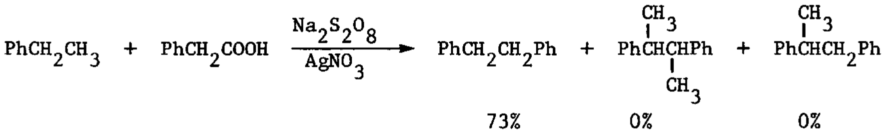
[a] Conversion is based on unreacted starting material recovered from the reaction mixture.
[b] Yield is based on recrystallized product. Identity was confirmed by comparison of IR, NMR, MS, and mp or GC retention time with literature data or an authentic sample.

salt. Entry 2 illustrates an example where a 1:1 mixture of meso:d,ℓ was obtained. This result is reminiscent of other radical dimerization procedures[8] and differs from more nucleophilic coupling processes which give ratios of > 10:1, meso:d,ℓ.[9]

Since the benzylic radical may be produced by either single electron transfer oxidation of the aromatic system or the carboxylate functionality, the following experiments were performed. Ethylbenzene was treated with the usual oxidant in refluxing aqueous acetonitrile, and it produced the coupled product, 1,2-diphenylbutane, (1:2, meso:d,ℓ) with a 40% conversion. This silver(II) catalyzed dimerization of ethylbenzene is itself an improvement over the previous yield of coupled product without a catalyst (5%).[10] When an equimolar mixture of ethylbenzene and phenylacetic acid was treated with 2 mole % silver nitrate and one half the usual oxidant, however, only diphenylethane was produced (55% conversion, 73% yield by GC). Unreacted ethylbenzene was recovered quantitatively. Thus the silver(I)/persulfate oxidation system selectively oxidizes the arylacetic acid molecule in the presence of a more electron rich aromatic ring. Because the ionization potential of phenylacetic acid (9.1 eV) is higher than ethylbenzene (8.76 eV) this suggests the carboxylic acid group is the site of oxidation.[11]



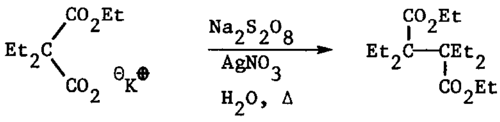
$$PhCH_2CH_3 \xrightarrow[AgNO_3,\ \Delta]{Na_2S_2O_8} PhCH(CH_3)-CH(CH_3)Ph$$



$$PhCH_2CH_3 + PhCH_2COOH \xrightarrow[AgNO_3]{Na_2S_2O_8} \underset{73\%}{PhCH_2CH_2Ph} + \underset{0\%}{PhCH(CH_3)CH(CH_3)Ph} + \underset{0\%}{PhCH(CH_3)CH_2Ph}$$

Selective oxidation of the carboxylate group of $PhCH_2COO^-$ in the presence of a copper(II)/persulfate oxidation system has been reported,[12] as well as the non-selective oxidation of the aromatic ring in 4-phenylbutanoic acid with cobalt(II) catalysis.[13] Oxidation at a carboxylate anion is therefore possible with several catalytic persulfate systems (Ag, Cu, Fe[14]), and is in accord with the known lower reduction potential of an acid salt when compared to the corresponding acid. Selective oxidation of arylacetic acids (in the acid form), however, only appears possible with the silver catalyst.[15] We have also observed that 4-phenylbutanoic acid is oxidized at both the aromatic ring and carboxylate group with the silver(I)/persulfate catalyst system.

The decarboxylative dimerization also proceeded, although in lower yield (30%), for the stabilized radical from $Et_2C(CO_2Et)CO_2K$ as shown below.



$$Et_2C(CO_2Et)CO_2^{\ominus}K^{\oplus} \xrightarrow[AgNO_3,\ H_2O,\ \Delta]{Na_2S_2O_8} Et_2C(CO_2Et)-C(CO_2Et)Et_2$$

General Dimerization Procedure. The carboxylic acid or potassium acid salt (1.29 mmoles) and silver nitrate (0.025 mmole) were dissolved in distilled water (15 mL) and heated to reflux. To this solution was added a solution of sodium persulfate (2.58 mmoles) in distilled water (10 mL) over fifteen minutes, and refluxing was continued for an additional five minutes. The reaction mixture was filtered, and the insoluble dimeric product recrystallized. Unreacted starting material was recovered by acidification and ether extraction of the aqueous reaction mixture.

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