H, 10.21. Found: C, 78.04; H, 10.13.

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Cobalt(III)-Catalyzed Trifluoroacetoxylation of Benzene

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The one-step oxidation of benzene directly to phenol has been the subject of much study. Hydroxylations have been performed using vanadium(V) peroxo complexes,[1] irradiation of powdered titanium dioxide,[2] aerial oxidation in the presence of Cu(I),[3] H_2O_2 in HF/BF_3,[4] Ni(II)–O_2 macrocyclic polyamine complexes,[5] and electroreduction of O_2 in the presence of Fe(II),[6] i),[6] $S_2O_8^{2-}$/Fe(II)/Cu(II),[7] Fenton's reagent (Fe(II)/H_2O_2),[8] and other Fe-based hydroxylation catalysts.[9] Further oxidation of the phenol product under these reaction conditions is often responsible for the low to moderate yields of phenol obtained, and the systems that generate hydroxyl radicals often also produce biphenyl as a byproduct. An alternate approach to that of hydroxylation is the acetoxylation or trifluoroacetoxylation of benzene, followed by hydrolysis; Co(III), Pb(IV), Mn(III), Ce(IV), Cu(II), and Tl(III) have been used as stoichiometric oxidants,[10] and Pd(II) and Ag(II) have been employed either stoichiometrically or as catalysts where product yields based on benzene reacted or oxidant consumed have been only fair.[10,11] We now report the production of phenol via the reaction of benzene and a peroxide or peracid oxidant (vide infra) with a cobalt(III) catalyst in trifluoroacetic acid/trifluoroacetic anhydride to produce phenyl trifluoroacetate; hydrolysis of this product yields phenol and solvent trifluoroacetic acid quantitatively.

Kochi and co-workers have previously reported the stoichiometric oxidation of benzene with cobalt(III) trifluoroacetate in trifluoroacetic acid/trifluoroacetic anhydride to produce phenyl trifluoroacetate (eq 1).[12] The

$$C_6H_6 + 2Co^{III}(O_2CCF_3)_3 \rightarrow C_6H_5O_2CCF_3 + 2Co^{II}(O_2CCF_3)_2 + CF_3CO_2H \quad (1)$$

yield of product was almost quantitative when the molar ratio of Co(III) to benzene was approximately 2. The reaction was proposed to proceed by a reversible one-electron transfer from benzene to Co(III) to produce a benzene radical cation, nucleophilic attack on the radical cation by solvent trifluoroacetic acid, and subsequent one-electron transfer to an additional 1 equiv of Co(III) to form phenyl trifluoroacetate. This mechanism was used to explain the high yields of product obtained, since the trifluoroacetate group deactivates phenyl trifluoroacetate toward oxidation by Co(III). The relative stability of the product to the strongly oxidizing reaction conditions prompted us to examine the possibility of using a peroxyacid or hydrogen peroxide as an oxidant to regenerate Co(III) from Co(II) for this same reaction (eq 2), eliminating the use of stoichiometric quantities of Co(III) trifluoroacetate.

$$ROOH + 2Co^{II}(O_2CCF_3)_2 + 2CF_3CO_2H \rightarrow ROH + 2Co^{III}(O_2CCF_3)_3 + H_2O \quad (2)$$

$$R = H,\ CF_3CO,\ CH_3CO$$

Results and Discussion

Table I lists representative examples of catalytic oxidations of benzene to phenyl trifluoroacetate using several different oxidants. Reactions were generally run in trifluoroacetic acid (TFA) containing 1-20% (v) trifluoroacetic anhydride (TFA-A), as it has been demonstrated that yields are higher under anhydrous conditions for stoichiometric oxidations of benzene by Co(III).[12] The highest product yields based on both converted benzene and added oxidant were obtained with trifluoroperacetic acid, which is readily prepared from hydrogen peroxide and trifluoroacetic anhydride in either dichloromethane[13] or trifluoroacetic acid. The presence of dichloromethane does not interfere with the course of the reaction; using either 10% (v) TFA-A in TFA or a 1:1 mixture of CH_2Cl_2 and 10% TFA-A in TFA as solvent for the stoichiometric oxidation of benzene by 2 equiv of cobalt(III) trifluoroacetate resulted in a 97% yield of phenyl trifluoroacetate.

Slow addition of the oxidant, either by the addition of aliquots of the oxidant sufficient to reoxidize the catalyst or by continuously adding the oxidant by syringe pump, resulted in higher product yields when using catalytic amounts of cobalt(II) acetate. For example, when 10 equiv (relative to cobalt) of trifluoroperacetic acid was added by syringe pump to a TFA/TFA-A solution 0.02 M in Co(II) and 0.1 M in benzene over a period of 20 h (Table I, entry 2), phenyl trifluoroacetate was produced in 96% yield based on benzene reacted, and oxidant selectivity was 70%; when this same reaction was repeated and all the oxidant was added at the start of the reaction, the product selectivity was only 3% at similar conversions and oxidant

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Table I. Product and Oxidant Selectivities for the Production of Phenyl Trifluoroacetate via the Cobalt(III)-Catalyzed Trifluoroacetoxylation of Benzene[a]

entry	oxidant	oxidant, mmol	Co(II), mmol	C_6H_6, mmol	time, h	conversion, %	product selectivity,[b] %	oxidant selectivity,[c] %	TN[d]
1	CF_3CO_3H/TFA	0.49	1.0	0.53	2	79	88	75	0.7
2	CF_3CO_3H/TFA	5.0	1.0	5.5	27	58	96	70	6
3	CF_3CO_3H/CH_2Cl_2	0.051	0.10	0.072	3	54	88	71	0.7
4	CF_3CO_3H/CH_2Cl_2	0.88	0.10	0.54	72	100	55	33	6
5	35% CH_3CO_3H	1.5	0.11	1.1	72	66	88	45	12
6[e]	30% H_2O_2	0.50	1.0	0.51	18	20	60	12	0.1
7[e]	30% H_2O_2	5.0	1.0	1.0	72	52	51	5.5	0.5
8	70% H_2O_2	0.50	1.0	0.53	2	9	53	4.6	0.05
9[f]	CH_3CHO/O_2	1.0	0.24	0.98	16	63	35	*g*	1.8
10[h]	CH_3CHO/O_2	1.0	0.23	0.92	5	53	33	*g*	1.5

[a] Reactions run at room temperature and in 10% (v) trifluoroacetic anhydride (TFA-A)/trifluoroacetic acid (TFA), unless otherwise noted. [b] Yield of phenyl trifluoroacetate based on reacted benzene. [c] Yield of phenyl trifluoroacetate based on added oxidant. [d] TN (turnover number) = (mmol of phenyl trifluoroacetate produced/mmol of Co(II) used) × 2 (see eq 1). [e] Reaction run in 20% TFA-A/TFA. [f] Reaction performed in 10 mL of trifluoroacetic acid at 60 °C and 1000 psi O_2. [g] Not determined. [h] Reaction performed in 10 mL of trifluoroacetic acid at 80 °C and 1000 psi O_2, using 0.11 mmol of cobalt(II) acetate and 0.12 mmol of cobalt(III) acetate as catalyst.

selectivity was only 1%. At concentrations of benzene greater than 0.4–0.5 M the selectivity to phenyl trifluoroacetate decreased markedly, possibly due to oxidative condensation of benzene to produce biphenyl, which is itself rapidly oxidized under these reaction conditions.[12] All of the reactions reported in Table I were performed with an initial benzene concentration of 0.1–0.2 M; the initial concentration of cobalt(II) was then chosen to effect the desired number of catalyst turnovers.

Peracetic acid is also capable of regenerating Co(III) trifluoroacetate from Co(II),[14] but the yield of product based on added oxidant was somewhat less than that obtained with trifluoroperacetic acid. One problem that may arise from using this oxidant is that, in addition to phenyl trifluoroacetate, phenyl acetate may be produced, and phenyl acetate will rapidly undergo further oxidation under these reaction conditions. Also, commercially available 35% peracetic acid contains significant amounts of water, which requires the presence of additional anhydride to prevent hydrolysis of phenyl trifluoroacetate to the more readily oxidized phenol.

Direct addition of hydrogen peroxide to a TFA/TFA-A solution of Co(II) and benzene gave 50–60% selectivity to phenyl trifluoroacetate, but very low (5–12%) yields of product based on added oxidant (Table I, entries 6–8). Because a large excess of anhydride relative to the amount of hydrogen peroxide added was present, it was anticipated that the hydrogen peroxide would react with the anhydride to form trifluoroperacetic acid in situ, and product and oxidant selectivities similar to those for direct addition of trifluoroperacetic acid would be obtained; this was not the case. The lower oxidant selectivities obtained for hydrogen peroxide compared to peracids is most likely due to the fact that unlike peracids, which are relatively stable toward decomposition in the presence of Co(III),[15] H_2O_2 is rapidly decomposed to water and oxygen by Co(II)/Co(III).[16] Also, because 30% or 70% aqueous hydrogen peroxide solutions were used, it is possible that the added water hydrolyzed phenyl trifluoroacetate, allowing further oxidation of the product to occur.

After demonstrating that phenyl trifluoroacetate could be produced from benzene by regenerating a catalytic amount of Co(III) with trifluoroperacetic or peracetic acid, catalyst regeneration via the in situ generation of peracetic acid from acetaldehyde and oxygen was examined. The oxidation of acetaldehyde with oxygen in the presence of cobalt(II) and cobalt(III) acetates to produce peracetic acid and/or acetic acid is well-known.[17] Scheme I depicts the series of reactions by which phenyl trifluoroacetate could be produced from benzene using CH_3CHO/O_2 as oxidant.

Scheme I

$$CH_3CHO + O_2 + 2Co^{II}(O_2CCF_3)_2 + 2CF_3CO_2H \rightarrow CH_3CO_2H + 2Co^{III}(O_2CCF_3)_3 + H_2O$$

$$C_6H_6 + 2Co^{III}(O_2CCF_3)_3 \rightarrow C_6H_5O_2CCF_3 + 2Co^{II}(O_2CCF_3)_2 + CF_3CO_2H$$

$$\text{net:}\quad C_6H_6 + CH_3CHO + CF_3CO_2H + O_2 \rightarrow C_6H_5O_2CCF_3 + CH_3CO_2H + H_2O$$

The cooxidation of benzene and acetaldehyde to produce phenyl trifluoroacetate and acetic acid, respectively, was run between room temperature and 150 °C with oxygen at 150–1000 psi; the best results are listed in Table I. Product selectivities and conversions were found to decrease with increasing concentration of trifluoroacetic anhydride, and in most cases the acid alone was used as the solvent. Significant amounts of other unidentified products and solids were often also produced in these reactions, especially at reaction temperatures greater than 100 °C, where conversions of benzene were high but selectivities to phenyl trifluoroacetate were no greater than 6%. Although the cooxidation of benzene and acetaldehyde to the desired products has been demonstrated, a number of problems are yet to be solved: (1) water produced by the reaction can hydrolyze phenyl trifluoroacetate to phenol (which can undergo further oxidation), but adding TFA-A to the TFA solvent inhibits the reaction and lowers selectivity; (2) the peracetic acid produced as an intermediate in the formation of acetic acid from acetaldehyde (and responsible to the reoxidation of Co(II)) can react directly with acetaldehyde to produce acetaldehyde monoperacetate or 2 equiv of acetic acid,[17] thus reducing the selectivity of the oxidant for phenyl trifluoroacetate production.

Experimental Section

General Remarks. *Extreme caution should be taken when working with peroxides or peracids.*[18] No metalware (e.g., syringe

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needles) should be employed. Only all-glass reaction vessels, gas-tight syringes with Teflon luer-lock hubs, and Teflon syringe needles and cannulas were used. Peroxytrifluoroacetic acid was prepared only as needed according to a modification of a literature procedure,[13] where 30% H_2O_2 was substituted for 90% H_2O_2 and, for some cases, trifluoroacetic acid[19] was substituted for dichloromethane as solvent. Benzene (thiophene free) was distilled from sodium/benzophenone under argon before use. Cobalt(II) acetate, trifluoroacetic acid, trifluoroacetic anhydride, acetaldehyde, 35% peracetic acid, and 30% H_2O_2 were obtained from commercial sources and used as received; a sample of 70% H_2O_2 (Albone 70) was obtained from DuPont. Benzene[20] and trifluoroacetic acid[21] are both toxic and should be handled with appropriate care. Cobalt(III) acetate was prepared by ozonation of cobalt(II) acetate and converted to cobalt(III) trifluoroacetate by ligand exchange in mixtures of trifluoroacetic acid and trifluoroacetic anhydride.[12,22] Reactions using acetaldehyde/oxygen as oxidant were performed in a Parr Model 4740 Hastelloy C high-pressure bomb. Product yields were determined by gas chromatography; analyses were performed on a Varian 3700 gas chromatograph using a 6-m 15% Apiezon L on Chromosorb W column, and mass spectral analyses were performed on a Finnigan 4000 GC/MS using a 30-m Durabond-1 medium-bore capillary column.

Trifluoroperacetic Acid as Oxidant. To a solution of benzene (0.428 g, 5.49 mmol) and cobalt(II) acetate (0.179 g, 1.01 mmol) in 50 mL of trifluoroacetic acid/10% trifluoroacetic anhydride at 25 °C was added 10 mL of a 0.5 M solution of trifluoroperacetic acid in trifluoroacetic acid/10% trifluoroacetic anhydride (cooled to 0 °C) by syringe pump over 20 h with stirring. The reaction mixture was initially a reddish pink that turned to dark green-black upon addition of the peracid. After the addition was complete, the reaction mixture was stirred an additional 7 h; completion of the reaction was indicated by the reddish brown color of the reaction mixture. Testing a sample of this reaction mixture with potassium iodide–starch test paper (Fisher) indicated that all the trifluoroperacetic acid had been consumed. The solution was then directly analyzed by gas chromatography using *n*-octane as an internal standard. The yield of phenyl trifluoroacetate was 56%, with a 58% conversion of benzene (selectivity to phenyl trifluoroacetate 96%). Oxidant selectivity (70%) was calculated from the yield of phenyl trifluoroacetate and the amount of oxidant consumed. Addition of water to the reaction mixture resulted in the quantitative conversion of phenyl trifluoroacetate to phenol and trifluoroacetic acid solvent.

The experiment above was repeated without the addition of cobalt(II) acetate to the reaction mixture, and only a 4.6% yield of phenyl trifluoroacetate was obtained.[23]

Peracetic Acid as Oxidant. A solution of benzene (0.043 g, 0.548 mmol) and cobalt(II) acetate (0.0187 g, 0.106 mmol) in 5 mL of trifluoroacetic acid/10% trifluoroacetic anhydride was stirred at 25 °C, and 0.010 mL of 35% peracetic acid (0.052 mmol) and 0.017 mL (0.12 mmol) of trifluoroacetic anhydride were added every 30 min for 10 h. An additional 0.042 g (0.54 mmol) of benzene was added to the solution, and eight more additions of peracetic acid and trifluoroacetic acid anhydride were added before the reaction was analyzed by gas chromatography using *n*-octane as internal standard. The yield of phenyl trifluoroacetate was 58%, with a 65% conversion of benzene (selectivity 89%).

Hydrogen Peroxide (30%) as Oxidant. To a solution of cobalt(II) acetate (0.177 g, 1.00 mmol) and benzene (0.0401 g, 0.51 mmol) in 5.0 mL of trifluoroacetic acid/20% trifluoroacetic anhydride at 0 °C was added 0.051 mL (0.50 mmol) of 30% hydrogen peroxide, and the solution stirred at 25 °C for 18 h. The resulting solution was analyzed by gas chromatography using *n*-octane as internal standard. The yield of phenyl trifluoroacetate was 12%, with a 20% conversion of benzene (selectivity 60%).

Acetaldehyde/Oxygen as Oxidant. Into a Parr bomb equipped with glass liner and Teflon-coated magnetic stirring bar were placed cobalt(II) acetate (0.0418 g, 0.236 mmol), benzene (0.0763 g, 0.98 mmol), acetaldehyde (0.044 g, 1.00 mmol), and 10 mL of trifluoroacetic acid. The bomb was pressurized to 1000 psi with oxygen and heated to 60 °C with stirring for 16 h. The yield of phenyl trifluoroacetate was 22%, with a 63% conversion of benzene (selectivity 35%).

Registry No. C_6H_6, 71-43-2; C_6H_5OH, 108-95-2; $(CF_3CO_2)_3CO$, 50517-80-1; $C_6H_5O_2CF_3$, 500-73-2.

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Propionyl and *n*-Butyryl Hypobromites and Hypoiodites as Intermediates in the Mercuric Propionate and *n*-Butyrate Induced Halogenation of Alkylbenzenes

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In studying the kinetics of the electrophilic attack of acetyl hypobromite and hypoiodite on aromatic hydrocarbons in acetic acid the use of solutions of mercuric acetate and bromine or iodine as the source of the highly reactive[1] acyl hypophalites has proved convenient.[2,3] In such solutions equilibria of the type shown in eq 1 are established. Equilibrium constants for the reactions (eq 2) can readily be obtained by a spectrophotometric method.

$$\mathrm{Hg(OC({=}O)R)_2 + X_2 \rightleftarrows Hg(OC({=}O)R)X + RCOOX} \qquad (1)$$

$$K_{\mathrm{RCOOX}} = \mathrm{[Hg(OCOR)X][RCOOX]/[Hg(OCOR)_2][X_2]} \qquad (2)$$

The consumption of halogen by aromatic substances in such mixtures can also be followed by a spectrophotometric method. The equilibrium constants are then used to calculate [RCOOX] values from halogen concentrations during the course of the runs, and rate constants k are evaluated on the assumption that reaction proceeds according to the rate law in eq 3, where $[X_2]_T$ is the sum of the concentrations of free halogen and acyl hypohalite in the reaction mixtures.

$$d[\mathrm{ArX}]/dt = -d[X_2]_T/dt = k[\mathrm{ArH}][\mathrm{RCOOX}] \qquad (3)$$

The equilibrium constant for the reaction of mercuric acetate and iodine in acetic acid is somewhat higher than

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