2974-90-5; 4-$ClC_6H_4C_6H_4$-4′-Cl, 2050-68-2; 4-$ClC_6H_4C_6H_4$-2′-OMe, 53824-23-0; 4-$ClC_6H_4C_6H_4$-3′-OMe, 66175-36-8; 4-$ClC_6H_4C_6H_4$-4′-OMe, 58970-19-7; 3,4-$Cl_2C_6H_3Ph$, 2974-92-7; 4-$BrC_6H_4C_6H_3$-2′,5′-Me_2, 89346-51-0; 4-$BrC_6H_4C_6H_2$-2′,4′,6′-Me_3, 20434-38-2; 2-MeC_6H_4Ph, 643-58-3; 3-MeC_6H_4Ph, 643-93-6; 4-MeC_6H_4Ph, 644-08-6; 4-$MeC_6H_4C_6H_4$-2′-Me, 611-61-0; 4-$MeC_6H_4C_6H_4$-3′-Me, 7383-90-6; 4-$MeC_6H_4C_6H_4$-4′-Me, 613-33-2; $Ph(CH_2)_2Ph$, 103-29-7; 3,4-$Me_2C_6H_3Ph$, 4433-11-8; 3,4-$Me_2C_6H_3C_6H_4$-2′-F, 89346-52-1; 3,4-$Me_2C_6H_3C_6H_4$-3′-F, 89346-53-2; 3,4-$Me_2C_6H_3C_6H_4$-4′-F, 72968-91-3; 4-EtC_6H_4Ph, 5707-44-8; 3,5-$(MeO)_2C_6H_3Ph$, 64326-17-6; 2-$O_2NC_6H_4Ph$, 86-00-0; 4-$O_2NC_6H_4Ph$, 92-93-3; 2-$O_2NC_6H_4CH{=}CHPh$, 4714-25-4; $PhCH_2P^+Ph_3Cl^-$, 1100-88-5; 2-$O_2NC_6H_4CHO$, 552-89-6; $PhCH{=}CHCH_2Cl$, 2687-12-9; Ph_3P, 603-35-0; 2-$O_2NC_6H_4Cl$, 88-73-3; PhS^-K^+, 3111-52-2; $PhO(CH_2CH_2O)_4Ph$, 20768-77-8; 2-$O_2NC_6H_4O(CH_2CH_2O)_4Ph$, 89346-79-2; 4-$O_2NC_6H_4O(CH_2CH_2O)_4Ph$, 89346-80-5; $HO(CH_2CH_2O)_4H$, 112-60-7; $PhCH_2Cl$, 100-44-7; $K^+{}^-O_2C(CH_2)_4CH_3$, 19455-00-6; $K^+{}^-O_2C(CH_2)_{14}CH_3$, 2624-31-9; CH_3CN, 75-05-8; KOAc, 127-08-2; NaOAc, 127-09-3; KO_2, 12030-88-5; K_2CO_3, 584-08-7; thiophene, 110-02-1; pyridine, 110-86-1; furan, 110-00-9; 2-phenylthiophene, 825-55-8; 2-phenylpyridine, 1008-89-5; 3-phenylpyridine, 1008-88-4; 4-phenylpyridine, 939-23-1; 2-(3-fluorophenyl)pyridine, 58861-54-4; 3-(3-fluorophenyl)pyridine, 79412-32-1; 4-(3-fluorophenyl)pyridine, 39795-59-0; 2-phenylfuran, 17221-37-3; 2-(4-chlorophenyl)thiophene, 40133-23-1; 2-(4-chlorophenyl)pyridine, 5969-83-5; 3-(4-chlorophenyl)pyridine, 5957-97-1; 4-(4-chlorophenyl)pyridine, 5957-96-0; 2-(4-bromophenyl)furan, 14297-34-8; 2-(4-bromophenyl)thiophene, 40133-22-0; 1*H*-indazole, 271-44-3; 2-(4-methylphenyl)furan, 17113-32-5; 2-(4-methylphenyl)pyridine, 4467-06-5; 3-(4-methylphenyl)-pyridine, 4423-09-0; 4-(4-methylphenyl)pyridine, 4423-10-3; 2-(4-nitrophenyl)furan, 28123-72-0; 2-(4-nitrophenyl)thiophene, 59156-21-7; 3,4-(methylenedioxy)benzenediazonium tetrafluoroborate, 1682-37-7; fluorenone, 486-25-9; phenanthrene-9-carboxylic acid, 837-45-6; dibenzo[*a*,*c*]cyclooctane, 1082-12-8; 3-(3-phenylpropyl)-1*H*-indazole, 89346-77-0; dibenzofuran, 132-64-9; dibenzothiophene, 132-65-0; 1,4,7,10,13-pentaoxa-14,15:16,17-dibenzocycloheptadecane, 89346-74-7; 2,5,8,11,14-pentaoxa-15,16:17,18-dibenzocyclooctadecan-1-one, 89346-75-8; 2-[2-[2-(2-benzoyloxyethoxy)ethoxy]ethoxy]ethoxybenzene, 89346-76-9.

Aromatic Acetonylation Promoted by Manganese(III) and Cerium(IV) Salts[1]

Michael E. Kurz,* Vijayalakshmi Baru, and P-Nhi Nguyen

Department of Chemistry, Illinois State University, Normal, Illinois 61761

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Treatment of aromatic hydrocarbons with acetone and manganese(III) acetate gave rise to arylacetones in yields ranging from 25% with chlorobenzene to 74% with anisole. Cerium(IV) salts were also successfully used as promoters but gave lower yields. The reactions were relatively free of side products except with toluene. Isomer distributions, relative rates, and partial rate factors were determined for acetonylation of anisole, toluene, chlorobenzene, and fluorobenzene. A Hammett plot of the log of the partial rate factors for the manganese(III) system vs. σ-constants gave a slope, ρ, of -2.4 ± 0.3. An isotope effect $k_H/k_D = 3.8$ was observed for the manganese(III)-promoted reaction with acetone-d_6, indicating rate-determining proton loss from acetone. The overall mechanism involves formation and attack of acetonyl radicals onto the aromatic hydrocarbon followed by subsequent oxidative deprotonation of the resulting σ-radical complex. The acetonyl radical exhibits appreciable electron-deficient character in its substitution behavior with aromatic hydrocarbons.

Metal ion promoted oxidative deprotonation methods have been used to generate such carbon radicals as the carboxymethyl,[2,3] acetonyl,[4,5] and nitromethyl[6-8] (eq 1).[9]

$$CH_3X \xrightarrow[Ce(IV)]{Mn(III)\ or} \cdot CH_2X + H^+ \qquad (1)$$

$$X = CO_2H,\ COCH_3,\ NO_2$$

When produced in the presence of suitable alkenes, quite a number of interesting processes have been reported,[2-5,10-12] most resulting from initial attack of the carbon radical onto the π-bond (eq 2). The analogous radical

$$RCH{=}CHR + \cdot CH_2X \rightarrow R\dot{C}HC(R)HCH_2X \qquad (2)$$

generation with aromatic hydrocarbons present has led to aromatic substitution (eq 3), the mechanism of which has

$$ArH + CH_3X \xrightarrow[Ce(IV)]{Mn(III)\ or} ArCH_2X \qquad (3)$$

been studied rather extensively for carboxymethylation[2] and nitromethylation.[6-8] However, the aromatic acetonylation has been described only briefly.[5,13] The purpose of this work was to more thoroughly study the metal ion promoted aromatic acetonylation with an eye toward assessing the polar properties of the acetonyl radical involved.

Experimental Section

Instrumentation. GC analyses were done on a Hewlett-Packard Model 5840A gas chromatograph equipped with a flame ionization detector and capillary inlet system (split mode). The capillary columns used were (1) 30 m × 0.22 mm sp 2100 glass, (2) 10 m × 0.22 mm sp 2100 glass, (3) 10 m × 0.22 mm Carbowax 20 M fused silica, and (4) 30 m × 0.22 mm bonded SE-30 fused

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silica column. Preparative GC was done on a Varian Aerograph Model 90-P gas chromatograph equipped with a 6 ft × 0.25 in. SS, 15% SE-30 on 80/100 Chromosorb W column. IR spectra were obtained with a Perkin-Elmer Model 710B spectrophotometer as thin films between sodium chloride discs or as solutions in chloroform-*d* using 0.1-mm sodium chloride matched cavity cells. NMR spectra were obtained with a 60-MHz Hitachi Perkin-Elmer Model R-24 B spectrophotometer, using chloroform-*d* solvent containing ~1% Me_4Si. Elemental analyses were performed by Micro Analysis Inc.

Manganese(III) acetate was prepared according to a literature method[8,14] and analyzed for purity by iodometry. Cerium(IV) acetate was prepared from ozonolysis of cerium(III) salts in acetic acid[15] and was used without isolation.[8] Cerium(III) ammonium nitrate was commercially available in high purity. The aromatic hydrocarbons and solvents (AR grade) were checked by GC and used as received. Acetone-d_6 (Aldrich) was found to contain <1% hydrogen by NMR analysis.

Some authentic compounds were purchased and used directly, including phenylacetone, *o*-(methoxyphenyl)-, *m*-(methoxyphenyl)-, and (*p*-methoxyphenyl)acetone, (*o*-fluorophenyl)acetone, and (*p*-fluorophenyl)acetone (Aldrich). Other aryl ketones were synthesized from the corresponding aryl acetonitriles. (*o*-Methylphenyl)acetonitrile, (*m*-methylphenyl)acetonitrile, (*p*-methylphenyl)acetonitrile, (*m*-methoxyphenyl)acetonitrile, 1-naphthylacetonitrile, and 2-naphthylacetonitrile were commercially available (Aldrich), while (*m*-fluorophenyl)acetonitrile [^{1}H NMR ($CDCl_3$) δ 2.3 (s, 2 H), 7.7–6.5 (m, 4 H); IR (neat) 2190, 2250 (C≡N) cm^{-1}] was made from *m*-fluorobenzyl chloride and sodium cyanide in DMF.[16] Arylacetonitriles were converted to arylacetones in two steps: (1) condensation with ethyl acetate in base to form 1-aryl-1-cyanoacetones[17] and (2) hydrolysis of the nitrile function and decarboxylation of the resulting β-keto acid.[18]

A portion of the solid or liquid 1-aryl-1-cyanoacetones produced in this fashion was dried and the individual NMR and IR spectra were recorded.

1-(*m*-Methylphenyl)-1-cyanoacetone: ^{1}H NMR ($CDCl_3$) δ 7.45–7.15 (m 4 H), 4.65 (s, 1 H), 2.4 (s, 3 H), 2.2 (s, 3 H); IR ($CDCl_3$) cm^{-1} 1727 (C=O), 2237 (C≡N).

1-(*o*-Methylphenyl)-1-cyanoacetone: ^{1}H NMR ($CDCl_3$) δ 7.6–7.2 (m, 4 H), 4.88 (s, 1 H), 2.42 (s, 3 H), 2.29 (s, 3 H).

1-(*p*-Methylphenyl)-1-cyanoacetone: ^{1}H NMR ($CDCl_3$) δ 7.3 (s, 4 H), 4.55 (s, 1 H), 2.39 (s, 3 H), 2.25 (s, 3 H); IR ($CDCl_3$) 1730 (C=O), 2275 (C≡N) cm^{-1}.

1-(*m*-Fluorophenyl)-1-cyanoacetone: ^{1}H NMR ($CDCl_3$) δ 7.5–6.9 (m, 4 H), 4.64 (s, 1 H), 2.3 (s, 3 H); IR ($CDCl_3$) 1729 (C=O), 2244 (C≡N) cm^{-1}.

1-(*m*-Methoxyphenyl)-1-cyanoacetone: ^{1}H NMR ($CDCl_3$) δ 7.3–6.6 (m, 4 H), 4.2 (s, 1 H), 3.1 (s, 3 H), 2.0 (s, 3 H).

1-(β-Naphthyl)-1-cyanoacetone: ^{1}H NMR ($CDCl_3$) δ 8.1–7.2 (m, 7 H), 4.8 (s, 1 H), 2.25 (s, 3 H).

1-(α-Naphthyl)-1-cyanoacetone: ^{1}H NMR ($CDCl_3$) δ 8.2–7.47 (m, 7 H), 5.32 (s, 1 H), 2.22 (s, 3 H); IR ($CDCl_3$) 1727 (C=O), 2244 (C≡N) cm^{-1}.

1-(*p*-Chlorophenyl)-1-cyanoacetone: ^{1}H NMR ($CDCl_3$) δ 8.5 (q, 4 H), 5.3 (s, 1 H), 2.4 (s, 3 H); IR (Nujol) 2250 (C≡N) cm^{-1}.

The 1-aryl-1-cyanoacetones were hydrolyzed with concentrated sulfuric acid, water was added, and decarboxylation to the aryl acetones was accomplished by heating.[18] After isolation the NMR and IR spectra of each arylacetone was recorded.

(*m*-Methylphenyl)acetone: 99% pure by GC; ^{1}H NMR (CCl_4 + Me_4Si) δ 7.47–6.77 (m, 4 H), 3.55 (s, 2 H), 2.33 (s, 3 H), 2.05 (s, 3 H); IR ($CDCl_3$) 1711 (C=O) cm^{-1}. Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 81.95; H, 8.41.

(*o*-Methylphenyl)acetone: 93% pure by GC; ^{1}H NMR ($CDCl_3$) δ 7.5–7.2 (m, 4 H), 3.75 (s, 2 H), 2.3 (s, 3 H), 2.17 (s, 3 H); IR ($CDCl_3$) 1712 (C=O) cm^{-1}. Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.55; H, 8.16.

(*p*-Methylphenyl)acetone: 99% pure by GC; ^{1}H NMR ($CDCl_3$ + Me_4Si) δ 7.3–7.1 (m, 4 H), 3.62 (s, 2 H), 2.3 (s, 3 H), 2.1 (s, 3 H); IR (neat) 1719 (C=O) cm^{-1}. Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.81; H, 8.39.

(*m*-Fluorophenyl)acetone: 95% pure by GC; ^{1}H NMR ($CDCl_3$) δ 8.03–6.8 (m, 4 H), 3.72 (s, 2 H), 2.17 (s, 3 H); IR (neat) 1714 (C=O) cm^{-1}. Anal. Calcd for C_9H_9OF: C, 71.04; H, 5.96. Found: C, 70.59; H, 6.14.

1-Naphthylacetone: 90% pure by GC; ^{1}H NMR ($CDCl_3$) δ 8.1–7.25 (m, 4 H), 4.1 (s, 2 H), 2.1 (s, 3 H); IR ($CDCl_3$) 1712 (C=O) cm^{-1}.

2-Naphthylacetone: ^{1}H NMR ($CDCl_3$) δ 8.1–7.2, 3.82, 2.14; IR (neat) 1729 (C=O).

(*p*-Chlorophenyl)acetone: ^{1}H NMR ($CDCl_3$) δ 7.2 (q, 4 H), 3.6 (s, 2 H), 2.1 (s, 3 H); IR (neat) 1718 (C=O), 830 cm^{-1}.

(*m*-Chlorophenyl)acetone: ^{1}H NMR ($CDCl_3$) δ 7.3–7.1 (m, 2 H), 3.7 (s, 2 H), 2.1 (s, 3 H).

Aromatic Acetonylation Promoted by Manganese(III) Acetate. General Procedure. These reactions were carried out by refluxing a mixture of manganese(III) acetate (1.34 g, 5 mmol) (limiting reagent), the aromatic (15 mL), acetone (15 mL), and glacial acetic acid (25 mL) under a nitrogen atmosphere until the dark brown of manganese(III) acetate changed to pale pink of manganese(II) acetate. The time required for the completion of the reaction depended on the aromatic, as indicated in Table I. The reaction mixture was partitioned between ether (40 mL) and water (25 mL). The ether layer was separated and washed with water (25 mL) and then with 5% sodium carbonate solution (2 × 25 mL) to remove any remaining acetic acid. The ether solution was then dried over anhydrous sodium sulfate and concentrated for both qualitative and quantitative analysis. A slightly modified procedure with lesser amounts of solid aromatic hydrocarbons was used for naphthalene (5 g, 0.039 mol) and *p*-dimethoxybenzene (10 g, 0.072 mol), since the unreacted aromatics interfered in the extraction process. Reactions using cerium(IV) ammonium nitrate and cerium(IV) acetate[8] were run in basically the same fashion.

Competition Reactions. Benzene (15 mL), either toluene (15 mL) or anisole (10 mL), acetone (15 mL), and glacial acetic acid (25 mL) were refluxed with manganese(III) acetate (5 mmol) under nitrogen atmosphere until the color changed from brown to pale pink. The reaction mixture was then worked up as described earlier, and the products were analyzed by GC. Since the substitution products with fluorobenzene were not readily separated from benzene, the rate of fluorobenzene acetonylation relative to that of anisole was determined and from this the relative rates of fluorobenzene to benzene obtained by $(k_{fluorobenzene}/k_{anisole})(k_{anisole}/k_{benzene})$.

Isotope Effect Studies. One control experiment reacting benzene, acetone-d_6, and manganese(III) acetate was performed to see if any hydrogen exchange occurred under typical reaction conditions. The NMR spectrum of the resulting phenylacetone-d_5 product after the usual workup procedure showed no signals due to methyl or methylene protons at δ 2–4. The isotope effect study

Table I. Aromatic Acetonylation Yields from ArH-Acetone-Metal Salt

ArH	$ArCH_2COCH_3$ yield,[a] %	$Mn(OAc)_3$ time, min	$Ce(OAc)_4$ $ArCH_2COCH_3$ yield,[a] %
benzene	40	90	23[b]
toluene	51[c]	60	4[d]
anisole	74	45	41
chlorobenzene	25	*e*	
fluorobenzene	29	105	
naphthalene	77	25	
p-dimethoxybenzene	39	40	

[a] Based on 1 mol of product per 2 mol of metal ion promoter; average of two or more runs, ±2% or better. [b] With cerium(IV) ammonium nitrate, 22% phenylacetone was obtained. [c] Benzyl acetate was obtained as a side product. [d] Some minor byproducts, not identified. [e] Not determined.

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was carried out by refluxing together benzene (10 mL), acetone (10 mL), acetone-d_6 (10 mL), acetic acid (25 mL), and manganese(III) acetate (5 mmol). The resulting mixture was worked up as usual. NMR integration indicated ratios of aromatic to methyl protons in the phenylacetone product of 6.39:3 and 6.27:3 (duplicate runs). The aromatic signal in excess of 5:3 was attributed to $C_6H_5CD_2COCD_3$, and from this ratios of $C_6H_5CH_2COCH_3$:$C_6H_5CD_2COCD_3$ of 3.6 and 3.9 were determined. The ratios of aromatic:methylene integrations, 3.2 and 3.7, in both runs were used as a cross check on phenylacetone to phenylacetone-d_5 ratios.

Product Identification. The reaction mixtures containing the products after the usual workup were subjected to GC analysis. They were spiked with authentic products, and their gas chromatograms were studied for peak enhancement on at least two dissimilar columns. To ensure more definitive identification, the reactions were run on a larger scale. After the usual workup, the concentrated reaction mixtures were subjected to preparative GC to collect the products. The collected products were then analyzed by IR and NMR analysis, and the spectra were compared to those of the authentics where possible. In some cases (e.g., naphthalene), the reaction mixture was run through a column containing silica gel as stationary solid phase and eluted first with a 80:20 hexanes:chloroform solvent, which removed all of the unreacted naphthalene. Then the product was eluted with chloroform. The solvent was then removed, and the IR and NMR spectra of the product were obtained directly. In the case of *p*-dimethoxybenzene, the column chromatography process was followed by isolation with preparative GC. In this case, no authentic sample was available nor was it prepared. Therefore, the product identification as (2,5-dimethoxyphenyl)acetone was based on IR and NMR spectra of the collected products: ^1H NMR ($CDCl_3$ + Me_4Si) δ 7–6.65 (m, 3 H), 3.78 (s, 6 H), 3.65 (s, 2 H), 2.13 (s, 3 H).

Quantitative Analysis. Determination of Isomer Distributions of Products from Fluorobenzene, Anisole, and Toluene. The isomer distributions of *o*-(methoxyphenyl)-, *m*-(methoxyphenyl)-, and (*p*-methoxyphenyl)acetones were determined by GC (column 1). Column 4 was utilized to separate the (chlorophenyl)acetone isomers.

To determine the (methylphenyl)acetones, a combined GC–NMR analysis was used. Column 3 could separate meta from ortho and para isomers. In the NMR spectra the two methylene hydrogens and aromatic methyl group hydrogens from the ortho isomer were separated from the analogous signals for the combined meta and para isomers. Thus the GC and NMR analyses were combined together to find the complete isomer distributions.

To determine the (fluorophenyl)acetone distribution, IR was combined with GC. The GC traces (column 1) showed a separate peak for the ortho isomer, while the meta and para isomers appeared together. The IR spectra showed a peak at 1042 cm^{-1} due exclusively to the ortho isomer and a peak at 1522 cm^{-1} due exclusively to the para isomer. Standard solutions of five different combinations of *o*-(fluorphenyl)- and (*p*-fluorophenyl)acetones in carbon tetrachloride were prepared and analyzed by IR. The ratios of I_0/I at 1042 cm^{-1} relative to I_0/I at 1522 cm^{-1} were converted into absorbance units and plotted against the ratios of ortho to para concentrations, and a straight line was obtained. From this calibration curve, the ratios of concentrations of ortho to para isomers in the reaction mixtures were obtained. These values in combination with GC traces gave total isomer distributions.

The percent yield of the products were obtained by adding a known amount of internal standard, generally methyl benzoate, to the reaction mixture. A GC (usually column 1) of the mixture was then taken, and the areas of the products were compared with that of the standard. The yields were based on 1 mol of product per 2 mol of manganese(III) acetate.

Results and Discussion

Arylacetone substitution products were obtained upon refluxing a series of aromatic hydrocarbons with acetone and either manganese(III) acetate (limiting reagent) or cerium(IV) salts in acetic acid medium. The general reaction is shown in eq 4. The yields in the products are

$$ArH + CH_3COCH_3 + 2Mn(OAc)_3 \rightarrow ArCH_2COCH_3 + 2HOAc + 2Mn(OAc)_2 \quad (4)$$

summarized in Table I along with the reaction duration in the manganese(III) cases.

The products obtained from the above reactions were mainly the substituted arylacetones in yields ranging from 25 to 77%. They were identified by comparison to authentic arylacetones synthesized by an alternate route (eq 5 and 6).[16,17]

$$ArCH_2CN + CH_3CO_2C_2H_5 \xrightarrow[2.\ CH_3CO_2H]{1.\ C_2H_5ONa} ArC(CN)HCOCH_3 \quad (5)$$

$$ArC(CN)HCOCH_3 + H_2O \xrightarrow{H_2SO_4} ArCH_2COCH_3 + NH_3 + CO_2 \quad (6)$$

The Mn(III)-promoted acetonylations were essentially free of side products except in the case of toluene where benzyl acetate was found. The results are similar to what Vinogradov and co-workers had earlier observed for toluene and benzene[11] and later on for some additional aromatic hydrocarbons.[13] Slightly lower yields were observed when cerium(IV) salts were utilized. Byproducts became a serious problem with toluene–cerium(IV) ammonium nitrate.

By analogy to earlier carboxylmethylation studies,[19] an acetonylation mechanism involving the acetonyl radical generated by a one-electron oxidation of acetone by manganese acetate (eq 7) followed by its attack onto the

$$CH_3COCH_3 \xrightarrow[-Mn(II)]{Mn(III)} CH_3COCH_2\cdot \quad (7)$$

$$CH_3COCH_2\cdot + ArH \longrightarrow Ar(H)CH_2COCH_3 \quad (8)$$

I

$$I \xrightarrow[-Mn(II)]{Mn(III)} ArCH_2COCH_3 + H^+ \quad (9)$$

aromatic compound to produce a σ-radical complex (I, eq 8) had been proposed.[11] Oxidation of this radical complex by a second mole of manganese(III) acetate gives the corresponding cation, which rapidly loses a proton to yield the final product (eq 9). Cerium(IV) salts perform similar functions.

The benzyl acetate side product observed with toluene results from the side-chain abstraction of toluene by acetonyl radical (eq 10), producing benzyl radical which is

$$CH_3COCH_2\cdot + C_6H_5CH_3 \rightarrow C_6H_5CH_2\cdot + CH_3COCH_3 \quad (10)$$

$$C_6H_5CH_2\cdot \xrightarrow[-Mn(II)]{Mn(III)} C_6H_5CH_2 + \xrightarrow{OAc^-} C_6H_5CH_2OAc \quad (11)$$

further oxidized by a second mole of manganese(III) acetate to give benzyl acetate (eq 11). The results obtained from our work seen to be consistent with this scheme.

Isotope studies were carried out with acetone-d_6 in order to determine more details of the mechanism for the formation of acetonyl radical. A control reaction in which benzene was reacted with acetone-d_6 and manganese(III) acetate was performed to check for hydrogen exchange under the usual experimental conditions. The phenylacetone product obtained possessed only a signal in the

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Table II. Isomer Distributions and Relative Rates for Aromatic Acetonylation

aromatics	% isomer distribution[a] ortho	meta	para	relative[b] rates
toluene	66.0	20.0	14.0	5.3
anisole[c]	84.3	2.6	13.1	12.3
chlorobenzene	72.1	6.0	21.9	1.12
fluorobenzene	70.7	9.6	19.7	0.65[d]
naphthalene	92.1[e]	7.9		

[a] Average of two or more runs in good agreement. [b] Relative rates were measured with respect to benzene, $k_{ArH}/k_{C_6H_6}$. [c] The isomeric composition with Ce(IV) acetate was $o/m/p$ = 78.0/5.5/16.5. [d] Determined indirectly from $k_{C_6H_5F}/k_{C_6H_5OCH_3} \times k_{C_6H_5OCH_3}/k_{C_6H_6}$. [e] α = 92.1, β = 7.9.

aromatic region, consistent with the structure $C_6H_5CD_2C(O)OCD_3$, and indicating that no hydrogen exchange occurred. Following this control, benzene and manganese(III) acetate were reacted with excess equimolar amounts of acetone-d_6 and acetone. This reaction produced phenylacetone and phenylacetone-d_5 in a ratio of 3.8 ± 0.2 to 1. This isotope effect of 3.8 for this reaction carried out at 90 °C was somewhat less than that, 5.8, reported earlier for the oxidation of acetone with manganese(III) acetate at 60 °C in the absence of aromatic compounds.[20] The large isotope effect in both studies suggests that hydrogen is lost in a rate-determining step. One possible sequence involved enolization (eq 12) followed by electron-transfer oxidation

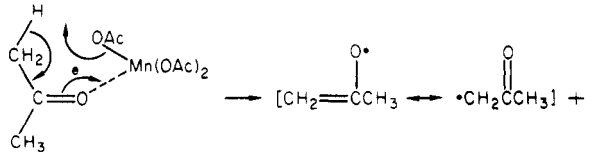
$$CH_3COCH_3 \rightleftharpoons CH_3C(OH)=CH_2 \quad (12)$$

$$CH_3C(OH)=CH_2 \xrightarrow[-Mn(II)]{Mn(III)} CH_3\overset{+\cdot}{C}(OH)-CH_2 \quad (13)$$

II

$$II \xrightarrow[slow]{-H^+} CH_3COCH_2\cdot \quad (14)$$

of the enol by manganese(III) (eq 13). Rate-determining proton loss from the resulting enol radical cation(II) forms the acetonyl radical (eq 14). A similar mechanism was proposed for the manganese(III) acetate promoted formation of *p*-methoxybenzyl radical from *p*-methylanisole[14] and nitromethyl radical from the aci form of nitromethane.[7] However, the rates of acetone oxidation have been shown to be faster than its rate of enolization.[20] An alternate mechanism (eq 15) involving concurrent proton



III

$$Mn(OAc)_2 + HOAc \quad (15)$$

and electron transfer by way of an intermediate complex (III) seems more consistent with the facts.[20]

The acetonylations of toluene, anisole, chlorobenzene, and fluorobenzene gave isomeric mixtures of disubstituted products. The isomer ratios (Table II) from chlorobenzene and anisole were determined by GC, whereas combined NMR and GC analysis was needed for the toluene isomers

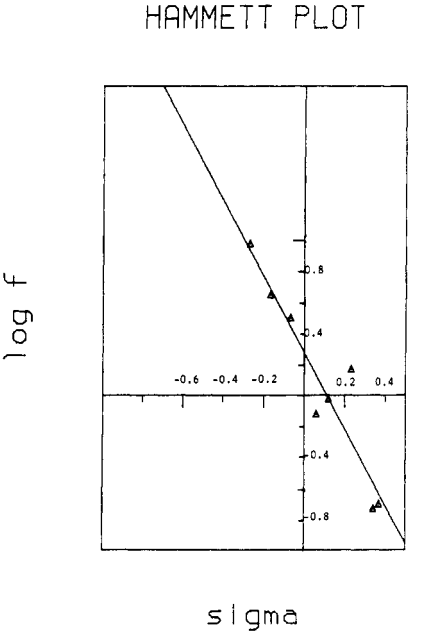


Figure 1.

Table III. Partial Rate Factors for Aromatic Acetonylation

ArX substituent, X =	partial rate factors ortho	meta	para
CH_3	10.5	3.2	4.5
OCH_3	31.1	0.96	9.7
F	1.4	0.19	0.77
Cl	2.6	0.20	1.5

and combined IR and GC was used for fluorobenzene. In all cases a fairly high proportion of ortho isomer was found, consistent with classical homolytic methylation[21] and phenylation[22] studies. Fairly similar (methoxyphenyl)-acetone mixtures were produced with cerium(IV) and manganese(III), suggesting an intermediate common to both.[8]

A series of competitions were run in which a mixture of either toluene, anisole, chlorobenzene, or fluorobenzene and usually benzene were allowed to compete for a limited amount of acetonyl radical generated from acetone and manganese(III) acetate. Relative rates of acetonylation were determined from the molar ratios of the two types of aryl acetones (Table II). Anisole and toluene were found to be significantly more reactive than benzene, chlorobenzene had about the same reactivity, and fluorobenzene was slightly less reactive. The relative rate determined for toluene considers only nuclear attack by the acetonyl radical and not side-chain hydrogen abstraction.

Partial rate factors were calculated (Table III). Hammett correlations were attempted by plotting the log of the meta and para partial rate factors vs. the substituent constants, σ or σ^+ (Figure 1). The plot obtained with σ yielded a ρ value (slope) of −2.4 ± 0.3 with a correlation coefficient σ = 0.94. A somewhat poorer fit (r = 0.87) resulted from the plot vs. σ^+ constants and the ρ value was −1.5 ± 0.3.

The reasonable correlation observed in the Hammet treatment is consistent with a reaction pathway involving the attack of acetonyl radical onto the aromatic compounds

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Table IV. Comparison of ρ^+ Values for Homolytic Aromatic Substitution

radical	ρ^+	ref
$C_6H_{11}\cdot$	1.1[a]	25
$CH_3\cdot$	0.1[a]	21
$C_6H_5\cdot$	0.1[a]	22
$\cdot CH_2CO_2H$	−0.6[b]	19
$\cdot CH_2COCH_3$	−1.5	this work
$\cdot CCl_3$	−1.5[b]	26
$\cdot CH_2NO_2$	−2.1	8
$C_6H_5CO_2\cdot$	−1.6	27
$i\text{-}C_3H_7OCO_2\cdot$	−2.3	28

[a] Plotted vs. ρ values, actually ρ. [b] Determined by hydrogen abstraction from substituted toluenes.

to produce a σ-radical intermediate (eq 8).[24] Many other homolytic aromatic substitutions have been nicely correlated by Hammett plots.[8,19,21,25] The large (−) ρ or ρ^+ values suggest that a fair degree of "+" charge develops on the aromatic ring during the substitution process and indicates that the acetonyl radical is electron deficient. As such it prefers attack on aromatics that have electron-donating substituents. This is evidenced by the higher yields obtained when either anisole or toluene is reacted with acetone compared to the yields obtained when either benzene or fluorobenzene is reacted (Table I).

A direct comparison of these ρ and ρ^+ values can be made to the nitromethyl radical produced from nitromethane and manganese(III), which gave values of −3.3 and −2.3, respectively.[8] For wide comparison purposes it is more informative to compare the ρ^+ values (despite the somewhat poorer correlation) with those from other electron-deficient radicals (Table IV), which generally have correlated better with σ^+ than σ. The ρ^+ values of −1.5 indicates that this radical is somewhat more electrophilic than the carboxymethyl radical,[19] despite the fact that it bears structural similarities (α-carbonyl group) to that radical. It is less electrophilic than the nitromethyl,[8] and a number of acyloxy radicals,[27,28] yet more so than most other carbon radicals.

Registry No. Benzene, 71-43-2; toluene, 108-88-3; anisole, 100-66-3; chlorobenzene, 108-90-7; fluorobenzene, 462-06-6; naphthalene, 91-20-3; *p*-dimethoxybenzene, 150-78-7; 1-(*m*-methylphenyl)-1-cyanoacetone, 38377-59-2; 1-(*o*-methylphenyl)-1-cyanoacetone, 75205-42-4; 1-(*p*-methylphenyl)-1-cyanoacetone, 27243-91-0; 1-(*m*-fluorophenyl)-1-cyanoacetone, 446-74-2; 1-(*m*-methoxyphenyl)-1-cyanoacetone, 25594-66-5; 1-(β-naphthyl)-1-cyanoacetone, 51074-12-5; 1-(α-naphthyl)-1-cyanoacetone, 31573-38-3; 1-(*p*-chlorophenyl)-1-cyanoacetone, 5219-07-8; (*m*-methylphenyl)acetone, 18826-61-4; (*o*-methylphenyl)acetone, 51052-00-7; (*p*-methylphenyl)acetone, 2096-86-8; (*m*-fluorophenyl)acetone, 1737-19-5; 1-naphthylacetone, 33744-50-2; 2-naphthylacetone, 21567-68-0; (*p*-chlorophenyl)acetone, 5586-88-9; (*m*-chlorophenyl)acetone, 14123-60-5; $Mn(OAc)_3$, 993-02-2; $Ce(OAc)_4$, 19475-87-7; D_2, 7782-39-0.

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Carbon–Hydrogen vs. Carbon–Carbon Bond Cleavage of 1,2-Diarylethane Radical Cations in Acetonitrile–Water[1]

Donald M. Camaioni* and James A. Franz

Battelle Pacific Northwest Laboratories, P.O. Box 999, Richland, Washington 99352

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Radical cations of 1,2-diarylethanes and 1-phenyl-2-arylethanes (Ar = phenyl, *p*-tolyl, *p*-anisyl) were generated in acidic 70% acetonitrile–water by Cu^{2+}-catalyzed peroxydisulfate oxidation. The radical cations fragment mainly by loss of benzylic protons (C–H cleavage) rather than by alkyl C–C bond cleavage. The 1,2-diarylethanol products undergo further selective oxidation to aryl aldehydes and arylmethanols via rapid equilibration of diarylethane and diarylethanol radical cations. The radical cation of 2,3-dimethyl-2,3-diphenylbutane fragments efficiently by C–C cleavage, forming cumyl radical and cumyl cation. Oxidations of bibenzyl–bicumyl mixtures show selective oxidation of bicumyl dependent on total substrate concentration, providing evidence of equilibrating radical cations and showing that bicumyl fragments faster than bibenzyl loses protons. The effects of reaction conditions and substrate structure on reactivity are discussed.

In 1973, Trahanovsky and Brixius reported that the Ce(IV) oxidation of 1,2-diarylethanes occurred by electron transfer to form radical cations which then undergo cleavage of the ethylene bond.[2] Since this study, the

$$[ArCH_2CH_2Ar]^{+\cdot} \rightarrow ArCH_2^+ + ArCH_2\cdot \quad (1)$$

formation and reactions of aromatic radical cations in solution have received much study.[3-10] One reaction found to be common for alkylbenzene radical cations involves dissociation to benzylic radicals and hydrogen ions.[3,5,8,9,11]

$$[PhCH_3]^{+\cdot} \rightarrow PhCH_2\cdot + H^+ \quad (2)$$

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