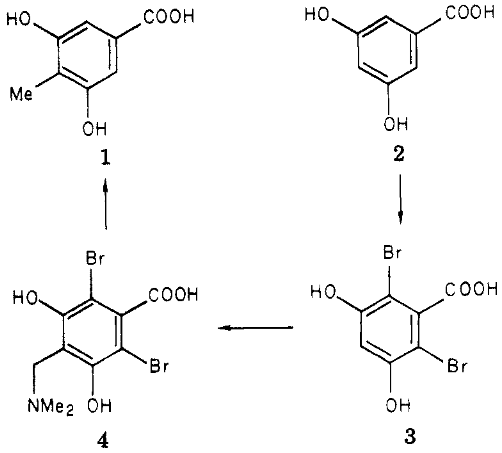
equiv) in chloroform to a suspension of **2** in chloroform at room temperature produced the dibromoresorcylic acid (**3**) in 97% yield. As the product precipitated from the reaction mixture, isolation was greatly simplified and entailed only filtration. Only trace amounts of the tribromo derivative of **2** were formed (as detected by mass spectrometry) presumably because of the insolubility of **3** in chloroform.



Next we considered the introduction of methyl group equivalents such as CH_2OH, CH_2Cl, or CH_2NMe_2 on C-4 of **3**, which would allow simultaneous generation of the methyl function and removal of bromines by, for example, catalytic hydrogenolysis. Attempts to hydroxymethylate or chloromethylate **3** were not successful, leading in each case to the formation of intractable products. However, when **3** was treated with 2 equiv of a mixture containing aqueous formaldehyde and aqueous dimethylamine in ethanol–acetic acid at toom temperature for 24 h, the Mannich base **4** precipitated and was isolated by filtration quantitatively. Similar results were obtained when morpholine was used as the amine. Presence of the (dimethylamino)methyl group in **4** could be easily detected by ^1H NMR. Treatment of **4** in 3 N NaOH with about equal weight of Raney nickel alloy at 25–30 °C resulted in the isolation of the desired benzoic acid **1** by extractive workup in 70% yield. Its physical properties were identical with those described in literature.[13] In addition, its ^1H NMR spectrum displayed, as expected, sharp singlets at δ 2.16 and 7.18 due to methyl and H-2 and H-6, respectively.

Experimental Section

2,6-Dibromo-3,5-dihydroxybenzoic Acid (3). To a stirred suspension of 3,5-dihydroxybenzoic acid (Aldrich, 97%, 38.1 g, 240 mmol) in 400 mL of chloroform was added from a pressure-equalizing dropping funnel a solution of bromine (80 g, 500 mmol) in 100 mL of chloroform at 25 °C over a period of 1.5 h. (A trap system leading from the top of the addition funnel was provided to trap evolving hydrogen bromide.) The mixture was then stirred at 25 °C for 5 h and filtered. The filter cake was washed with chloroform (3 × 100 mL) and then with ice cold water (1 × 200 mL). The precipitate was dried under vacuum over NaOH overnight to give 72.6 g (97%) of **3** as a white powder: mp 256 °C dec; ^1H NMR (acetone-d_6) δ 6.80 (s, H-4, after exchange of OH protons with D_2O); mass spectrum (EI), *m/e* (relative intensity) 314 (54, $M^+ + 4$), 312 (100, $M^+ + 2$), 310 (53, M^+).

Anal. Calcd for $C_7H_4Br_2O_4$: C, 26.95; H, 1.29. Found: C, 27.07; H, 1.33.

2,6-Dibromo-3,5-dihydroxy-4-[(dimethylamino)methyl]benzoic Acid (4). To a stirred mixture of 37% aqueous formaldehyde (76.8 g, 960 mmol), absolute ethanol (160 mL), and glacial acetic acid (320 mL) was added 40% aqueous dimethylamine (108 g, 960 mmol) in portions with cooling, keeping the temperature at ~25 °C. The cooling bath was removed and powdered 2,6-dibromo-3,5-dihydroxybenzoic acid (**3**; 149.8 g, 480 mmol) was added over a period of 2 min. The mixture became homogeneous and darkened slightly, and after ~5 min a white solid began to appear. The mixture was stirred at 25 °C for 24 h and then at 0 °C for 2 h (to complete precipitation of product) and filtered. The precipitate was washed with cold acetone (2 × 200 mL), dried under suction briefly (prolonged exposure to air darkens the product), and then under vacuum to give 173.6 g (98%) of **4** as a white powder: mp 210 °C dec; ^1H NMR (dimethyl-d_6 sulfoxide) δ 2.48 (s, 6 H, NMe_2), 4.00 (s, 2 H, CH_2), 5.50 (br s, OH, exchanged with D_2O); mass spectrum (EI), *m/e* (relative intensity) 371, (10, $M^+ + 4$), 369 (19, $M^+ + 2$), 367 (11, M^+).

Anal. Calcd for $C_{10}H_{11}Br_2NO_4$: C, 32.55; H, 3.00; N, 3.80. Found: C, 32.51; H, 3.35; N, 3.48.

3,5-Dihydroxy-4-methylbenzoic Acid (1). To a stirred solution of 2,6-dibromo-3,5-dihydroxy-4-[(dimethylamino)methyl]benzoic acid (**4**; 73.8 g, 200 mmol) in 500 mL of 3 N NaOH (1500 mmol) under nitrogen was added with cooling, keeping the temperature at 25–30 °C, in 3–4-g portions 69 g of Raney nickel alloy (Grace, No. 2813 Raney Nickel Catalyst Powder) over a period of 4 h. The mixture was then stirred at 25 °C for 12 h and filtered through a pad of Celite covered with a thin layer of glass wool. The filter cake was washed with water (2 × 100 mL), and the combined filtrates were acidified to pH 1 with concentrated HCl to give a clear pale yellow or light purple solution. The solution was extracted with ethyl acetate (4 × 75 mL), and the combined organic extracts were washed with 10% NaCl solution (2 × 30 mL), dried (Na_2SO_4), and evaporated in vacuo to dryness to give 23.24 g (70%) of **1** as a white solid: mp 264–265 °C (lit.[13] mp 264–265 °C); ^1H NMR (acetone-d_6) δ 2.16 (s, 3 H, CH_3), 5.35 (br s, OH, exchanged with D_2O), 7.18 (s, 2 H, H-2, H-6). Benzylation ($PhCH_2Cl/K_2CO_3$/DMF, 95 °C, 4 h) of **1** gave known benzyl 3,5-(dibenzyloxy)-4-methylbenzoate: mp 118–119 °C (lit.[9] mp 118–119 °C). The ^1H NMR of this benzoate was identical with that described in literature.[9]

Acknowledgment. The support of this work through a grant from the National Institute of Neurological and Communicative Disorders and Stroke (NS-15692) and a postdoctoral fellowship to A.K.S. from the American Heart Association—Kansas Affiliate is gratefully acknowledged.

Registry No. 1, 28026-96-2; **2**, 99-10-5; **3**, 79200-80-9; **4**, 79200-81-0; benzyl 3,5-(dibenzyloxy)-4-methylbenzoate, 76447-15-9.

$S_{RN}1$ Reactions of *o*-Dibromobenzene with Ketone Enolate Ions[1]

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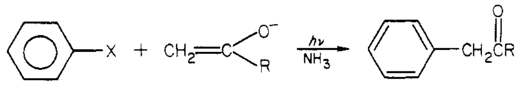
Under irradiation, ketone enolate ions in ammonia solution are phenylated by reaction with halobenzenes[3-5] (eq 1). There is evidence that these reactions occur by the radical-chain $S_{RN}1$ mechanism.[6]

 (1)

Several other nucleophiles also react with simple halobenzenes under photostimulation.[6]

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Scheme I

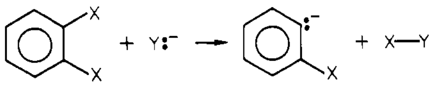
$$[XQX]^{-}\cdot \longrightarrow XQ\cdot + X^{-} \quad (M1)$$
$$XQ\cdot + Y^{-} \longrightarrow [XQY]^{-}\cdot \quad (M2)$$
$$[XQY]^{-}\cdot + XQX \longrightarrow XQY + [XQX]^{-} \quad (M3)$$
$$[XQY]^{-}\cdot \longrightarrow YQ\cdot + X^{-} \quad (M4)$$
$$YQ\cdot + Y^{-} \longrightarrow [YQY]^{-} \quad (M5)$$
$$[YQY]^{-}\cdot + XQX \longrightarrow YQY + [XQX]^{-}\cdot \quad (M6)$$

The reactions of dihalobenzenes with two of these, thiophenoxide ion and diethyl phosphite ion, have been investigated searchingly.[7-11] Photostimulated reactions of many *m*- and *p*-dihalobenzenes with PhS^- and $(EtO)_2PO^-$ afford high yields of disubstitution products. Furthermore, they provide evidence that for the most part monosubstitution products, in which one of the halogens has been replaced, are not intermediates on the way to disubstitution products. Such behavior, although it would be strange for other substitution mechanisms, is easily accommodated by the $S_{RN}1$ mechanism.[6] The propagation steps for reaction of a dihalobenzene (symbolized XQX, where Q stands for a divalent *o*-, *m*-, or *p*-phenylene group) with a nucleophile (symbolized Y^-) are presented in Scheme I.

In Scheme I, a short propagation cycle comprising steps M1, M2, and M3 leads to monosubstitution product XQY. A long cycle comprising steps M1, M2, M4, M5, and M6 affords disubstitution product YQY. It is noteworthy that monosubstitution product XQY appears only once in Scheme I, in step M3, and that step M3 is not a component of the long cycle leading to disubstitution product.

Some dihalobenzenes react with PhS^- or $(EtO)_2PO^-$ to form mainly monosubstitution products. That outcome is consistent with Scheme I for the case that step M3 is faster than step M4.

The situation with *o*-dihalobenzenes is more complicated because one halogen can activate nucleophilic attack on the other with resulting positive halogen transfer and release of an *o*-halophenyl anion (eq M7). Diethyl phosphite ions react rapidly with *o*-haloiodobenzenes in this way, in the dark, forming halobenzenes and benzyne-derived products.[11] When irradiation is started immediately upon mixing, substantial yields of arylphosphonate esters resulting from $S_{RN}1$ reactions are formed but they are accompanied by products of nucleophilic displacement on halogen in the manner of eq M7. Such complications are even more serious in reactions of diphenyl phosphide ion; this nucleophile undergoes satisfactory $S_{RN}1$ reactions with iodo- and bromobenzene to form triphenylphosphine[12] but its reactions with o-$C_6H_4X_2$ (X = I, Br, or Cl) fail to give any *o*-phenylenebis(diphenylphosphine).[13] The products that were obtained were interpreted to arise from initial nucleophilic attack of Ph_2P^- on halogen.[13] Similar complications have attended reactions of analogous stibide ions with *o*-dihalobenzenes.[14]



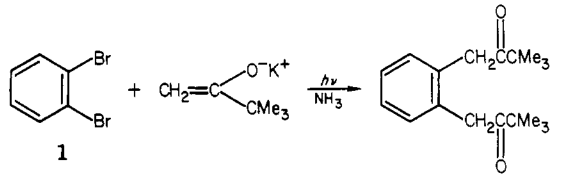
(M7)

Relatively little attention has been given to reactions of dihalobenzenes with ketone enolate ions. Alonso and Rossi[15] found *p*-dichlorobenzene to react under irradiation with pinacolone enolate ion to give 1,4-bis(3,3-dimethyl-2-oxobutyl)benzene in 65% yield, and similarly to react with acetone enolate ion to form a mixture of 1,4-bis(2-oxopropyl)benzene and a polymeric product. They reported *p*-dibromobenzene and *p*-bromoiodobenzene to behave similarly. Komin and Wolfe[16] observed 2,6-dibromopyridine and 2,6-dichloropyridine to undergo photostimulated reaction with pinacolone enolate ion in ammonia to form 2,6-bis(3,3-dimethyl-2-oxobutyl)pyridine in high yields. The fact that an interrupted reaction afforded only this disubstitution product and recovered 2,6-dichloropyridine, but no monosubstitution product, strongly suggested that the latter was not an intermediate in formation of the diketone product.

Our interests in studying reactions of *o*-dibromobenzene with ketone enolate ions were several. Would nucleophilic attack on bromine as depicted in eq M7 interfere with $S_{RN}1$ reactions? If not, would mono- or disubstitution predominate? Would polymers form? If disubstitution occurs, would intramolecular aldol condensation ensue to form indene derivatives (in analogy to a step in the formation of indoles by reactions of *o*-haloanilines with ketone enolate ions[17])?

Results and Discussion

Reaction with Pinacolone Enolate Ion. Reaction of *o*-dibromobenzene (1) with excess pinacolone enolate ion in ammonia, with irradiation for 2 h, afforded disubstitution product 2 in 62% yield. Unreacted 1 amounted to 35%, and there was no evidence of monosubstitution product or of any product that might be expected to result from nucleophilic attack of the enolate ion on bromine of 1. Thus straightforward disubstitution occurred, probably via the long cycle of propagation steps in Scheme I.



(2)

Reaction with Acetone Enolate Ion. Reaction of 1 with excess potassium acetone enolate, under irradiation for 3 h, followed by conventional workup, afforded 64% of a mixture of two acetylmethylindenes, probably 3 and 4, as well as a 5% yield of 9,10-diacetylanthracene (5). No polymer or (*o*-bromophenyl)acetone or product that could be attributed to nucleophilic attack on bromine was found.

One would anticipate that 4 would readily undergo prototropic rearrangement to 3. However, refluxing a portion of the product mixture with methanolic sodium methoxide with ensuing acidification did not alter the ratio of the two acetylmethylindene isomers. On the other hand, treatment with triethylamine effected isomerization so as to form the single isomer 3, which was obtained as a crystalline solid, mp 88–89 °C.

The obvious precursor of 3, 4, and 5 is the straightforward disubstitution product, *o*-diacetonylbenzene (6).

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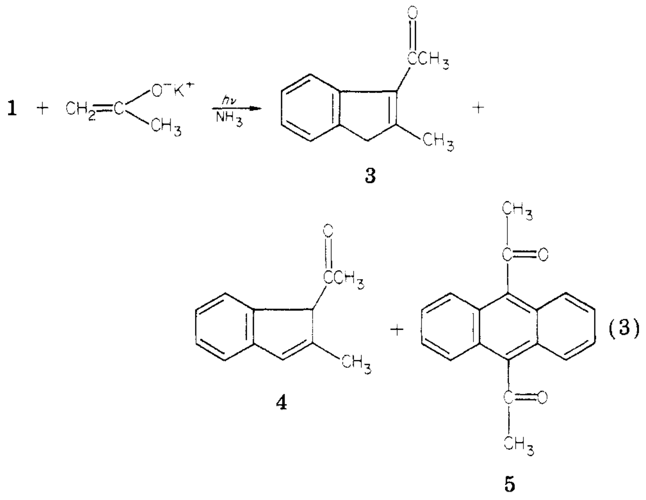
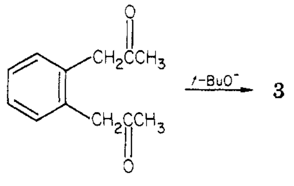




6

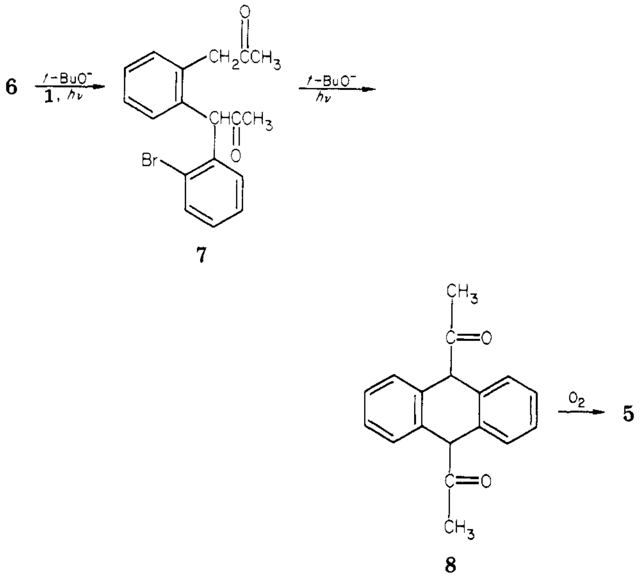
Under the strongly basic reaction conditions (with excess *tert*-butoxide ion present), **6** is converted to an enolate ion by loss of a proton from a site next to the benzene ring. The resulting carbanion readily attacks the carbonyl group of the other side chain and by a normal aldol condensation mechanism forms acetylmethylindene **3**. However, **3** is also converted into a carbanion under the highly basic reaction conditions. Protonation of it on workup evidently affords **3** and **4** in more or less equal amounts.

The same conjugate base of **3** is doubtless formed on treatment of **3** and/or **4** with $NaOCH_3$ in methanol, and it again gives a mixture of **3** and **4** on acidification. Triethylamine is however a base of strength such that it can only partially deprotonate **3** and/or **4**; it thereby effects equilibration between **3** and **4** as molecules, and **3** is overwhelmingly preponderant in the equilibrium. This is as one would expect from the studies of Friedrich and Taggart,[18] as well as from theoretical considerations.

The probable route to **5** (Scheme II) involves participation of the conjugate base of **6** as a nucleophile in $S_{RN}1$ reaction with another molecule of **1**. Such a second step of arylation of an arylacetone enolate ion is well precedented.[5,15] The resulting **7** is then converted to various enolate ions, one of which is well constituted for $S_{RN}1$ ring closure (for which there is also precedent[19,20]) to form dihydroanthracene derivative **8**. The latter is presumably oxidized to **5** by oxygen of the air during workup. In contrast, the isomer of **7** formed from *p*-dibromobenzene[15] cannot undergo further intramolecular $S_{RN}1$ reaction and instead reacts intermolecularly to afford an oligomer or polymer.

The fact that we obtained **2** cleanly from **1** and pinacolone enolate ion (eq 2) contrasts with the complexity of the products from acetone enolate ion (eq 3). The two *tert*-butyl groups in **2** evidently block both intramolecular aldol condensation and participation of the conjugate base of **2** in $S_{RN}1$ reaction with **1**.

Scheme II



In summary, the photostimulated reactions of *o*-dibromobenzene with ketone enolate ions appear to occur normally, giving disubstitution products directly via the long cycle of steps M1, M2, M4, M5, and M6 of Scheme I, without complications due to nucleophilic attack on halogen as in eq M7. Polymers are not formed, but the product diketone may, if steric factors permit, undergo intramolecular aldol condensation to form an indene or further arylation to form an anthracene derivative.

Experimental Section

Reaction of 1 with Potassium Acetone Enolate. Into a three-necked flask (500 mL) equipped with a cold-finger condenser (containing solid CO_2 in 2-propanol in its central well), a nitrogen inlet, and magnetic stirrer was condensed 300 mL of ammonia. To the ammonia was added a catalytic amount of ferric nitrate followed by potassium metal (2.34 g, 60 mmol). After the color of the solution had changed from blue to gray, acetone (2.32 g, 40 mmol), *tert*-butyl alcohol (1.61 g, 21.8 mmol), and *o*-dibromobenzene (2.36 g, 10 mmol) were added slowly and in succession. The entire assembly was placed in a Rayonet Model RPR-100 photochemical reactor equipped with 16 "350-nm" lamps and irradiated, with stirring, for 3 h but with interruption every 20 min to wipe accumulated frost from the outside of the flask. The flask was removed from the reactor, excess solid NH_4NO_3 was added and then 100 mL of diethyl ether, and the ammonia was allowed to escape. Sufficient water was added to dissolve the inorganic salts and the ether layer was separated. The aqueous layer was extracted twice with 50-mL portions of ether, and the combined ether extracts were washed with saturated aqueous NaCl and then dried over $MgSO_4$. GLC analysis showed a 4.5% yield of 9,10-diacetylanthracene (**5**), 5% of unreacted **1**, and, on the assumption of normal molar response factors, 64% of a mixture of two species of mass 172. These two species had identical mass spectra identical also with the mass spectrum of authentic **3** (see below). They are believed to be **3** and **4**. The combined ether extracts were concentrated by distillation; addition of petroleum ether (60–80 °C) to the residue caused precipitation of 9,10-diacetylanthracene (70 mg, 3%), mp 236–238 °C. It was recrystallized from methanol: mp 239–240 °C (lit.[21] mp 240 °C); NMR ($CDCl_3$) δ 2.78 (s, 6 H), 7.73–7.60 (m, 8 H); mass spectrum, *m/e* 262, 247, 219, 204, 189, 176. Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 81.85; H, 5.43.

A portion of the filtrate was treated with triethylamine at 40 °C for 2 h and then allowed to stand overnight. The major component was separated by preparative GC over 10% UC-W98

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J. Org. Chem. 1981, 46, 5025-5027

on Chromosorb B. The resulting solid was recrystallized from ether (mp 88-89 °C): NMR ($CDCl_3$) δ 2.42 (s, 3 H), 2.56 (s, 3 H), 3.52 (s, 2 H), 7.24-7.71 (m, 4 H); mass spectrum, m/e 172, 130, 119, 105, 43 (base peak). These data, with reference also to NMR spectra of related compounds,[22] serve to identify the substance as 2-methyl-3-acetylindene (**3**). However, this compound is not very stable. After standing for 3 days in a stoppered tube it changed to a liquid. The NMR spectrum now showed a singlet at δ 2.42 (3 H), a doublet at 3.11 (3 H), and a multiplet at 7.26-7.70 (4 H). There was a loss in the number of protons. The reaction mixture also showed a decreased percentage of the two isomers when examined after a few days. It is possible that these indene derivatives undergo oxidation on standing.

Reaction of 1 with Potassium Pinacolone Enolate. The procedure was identical with that used for reaction of **1** with potassium acetone enolate except that the irradiation time was 2 h. GLC analysis of the concentrated diethyl ether extracts showed formation of 62.5% of **2** and recovery of 34.6% of **1**. Addition of petroleum ether (60-80 °C) caused precipitation of 1,2-bis(3,3-dimethyl-2-oxobutyl)benzene (**2**) (0.84 g, 32%), mp 140-141 °C. After recrystallization from 90% acetone/10% water: mp 141-142 °C; NMR ($CDCl_3$) δ 1.3 (s, 18 H), 3.76 (s, 4 H), 6.9 (m, 4 H); mass spectrum, m/e 274, 189, 171, 161. Anal. Calcd for $C_{18}H_{26}O_2$: C, 78.79; H, 9.55. Found: C, 78.84; H, 9.63.

Registry No. 1, 583-53-9; **2**, 79201-31-3; **3**, 79201-32-4; **4**, 79201-33-5; **5**, 67263-73-4; **6**, 79201-34-6; **7**, 79201-35-7; **8**, 79201-36-8; potassium acetone enolate, 25088-58-8; potassium pinacolone enolate, 55440-76-1.

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Electronic Effects in Dienetricarbonyliron Derivatives. 3.[1] p-[(π-1,3-Butadiene)tricarbonyliron]benzoic Acid[2]

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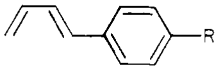
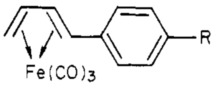
Received February 18, 1981

In an effort to evaluate the relative magnitude and character of the electronic properties of the dienetricarbonyliron system, the pK_a measurements of a series of para-substituted 1-phenyl-1,3-butadienes (**1a-c**) and their



1a, R = OH
b, R = NH_2
c, R = CO_2H



2a, R = OH
b, R = NH_2
c, R = CO_2H

tricarbonyliron complexes (**2a-c**) were studied. The results from the para-substituted anilines **1b** and **2b** were previously reported and discussed.[1] This paper reports the synthesis of acids **1c** and **2c** and the determination of their pK_a values.

Synthesis

The synthesis of **1c** and **2c** is shown in Scheme I. Starting with p-carboxybenzaldehyde (**3**) we obtained 1-[p-(carbomethoxy)phenyl]-1,3-butadiene (**5**) through ester formation followed by a Wittig reaction. Base hydrolysis of the ester gave the required p-(1,3-butadieneyl)benzoic acid (**1c**). Complexation of the olefin by using triiron dodecacarbonyl followed by base hydrolysis yielded the desired complexed acid **2c**. While the yields by this method were not high, all the steps were straightforward, and sufficient quantities of material were obtained for the pK_a studies.[3]

Table I. pK_a Values of Acids in 80% Ethanol at 25 °C

acid	apparent pK_a	acid	apparent pK_a
1c	4.45	$PhCO_2H$	6.50[a]
2c	5.05		

[a] Lit.[6] 6.78.

pK_a Study and Discussion

The relative magnitude and character of the electronic property of the dienetricarbonyliron system was obtained through pK_a studies. Use of this method with para-substituted benzoic acids is well-known:[4] the substitutent group is far from the reaction center, but participation by electron withdrawal or electron donation can still take place through the π system. Since the acids **1c** and **2c** were not completely soluble in water, apparent pK_a's were determined in aqueous ethanol (80% by volume) at 25 °C by titration with hydrochloric acid.[5] The data for **1c**, **2c**, and benzoic acid are presented in Table I.[6]

Both the diene and the dienetricarbonyliron groups are electron withdrawing with respect to hydrogen. Both weaken the O-H bond and increase the acidity. However, the tricarbonyliron group reduces the electron withdrawal of the simple diene, and, as previously observed,[1,7] the dienyltricarbonyliron group is less of an electron-withdrawing system than that of the diene. The overall effect, when only these two systems are compared, seems to be one of electron donation for the dienyltricarbonyliron system.

The electron-withdrawing properties of the diene system are in agreement with the observed electron withdrawal of similar groups. For example, Eaborn and co-workers[8] evaluated acetylene and 1,3-diyne groups as para substituents and found them to be electron withdrawing. Most likely all these unsaturated systems withdraw electrons by conjugation with the aromatic ring. The measured acidities shown in Table I indicate that the $Fe(CO)_3$ group is electron releasing. This most likely results from disruption of the conjugation of the dienyl group with the aromatic ring.[9] The disruption would be through backbonding and population of the antibonding orbitals of the dienyl system. Effectively, the $Fe(CO)_3$ system is changing the character of the dienyl system, a phenomenon not unusual when complexing occurs to a transition metal, and this is consistent with the models proposed by Pettit and Emerson[7] and Mahler.[10]

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[1] For paper 2 see J. M. Landesberg and L. Katz, *J. Organomet. Chem.* **33** C15-C16 (1971).

[2] This work was presented at METROCHEM'78, South Fallsburg, NY, Oct 6-9, 1978; Abstracts of Papers, p 8.

[3] Other routes using **2**, (R = Br, CN, or $COCH_3$) as starting material were unworkable; only polymeric residues were ever isolated. See J. M. Landesberg, L. Katz, and Carol Olsen, *J. Org. Chem.*, **37**, 930 (1972).

[4] J. Hine, "Physical Organic Chemistry", 2nd ed., McGraw-Hill, New York, 1962, Chapter 4.

[5] A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases", Wiley, New York, 1962, Chapters 1, 2.

[6] E. Grunwald and B. J. Berkowitz, *J. Am. Chem. Soc.*, **73**, 4939 (1951).

[7] R. Pettit and G. F. Emerson, *Adv. Organomet. Chem.*, **1**, 13 (1964).

[8] C. Eaborn, A. R. Thompson, and D. R. M. Walton, *J. Chem. Soc. B*, 357 (1970); C. Eaborn, A. R. Thompson, and D. R. Walton, *ibid.*, 859 (1969).

[9] G. Reichenback, G. Cardaci, and G. G. Aloisi, *J. Organomet. Chem.*, 134, 47 (1977), observed siimilar properties for the $Fe(CO)_4$ system.

[10] J. E. Mahler, Ph.D. Theis, University of Texas, Austin, TX, 1963.

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