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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(22) Craig, J. C.; Dinner, A.; Mulligan, P. J. *J. Org. Chem.* **1974**, *39*, 1669. Marx, J. N.; Cringle, D. C. *Syn. Commun.* **1973**, *3*, 95. Taylor, G. A.; Rakita, P. E. *Org. Magn. Reson.* **1974**, *6*, 644.

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

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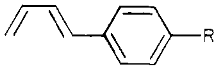
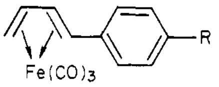
In an effort to evaluate the relative magnitude and character of the electronic properties of the dienetricarbonyliron system, the pK_a measurements of a series of para-substituted 1-phenyl-1,3-butadienes (**1a-c**) and their



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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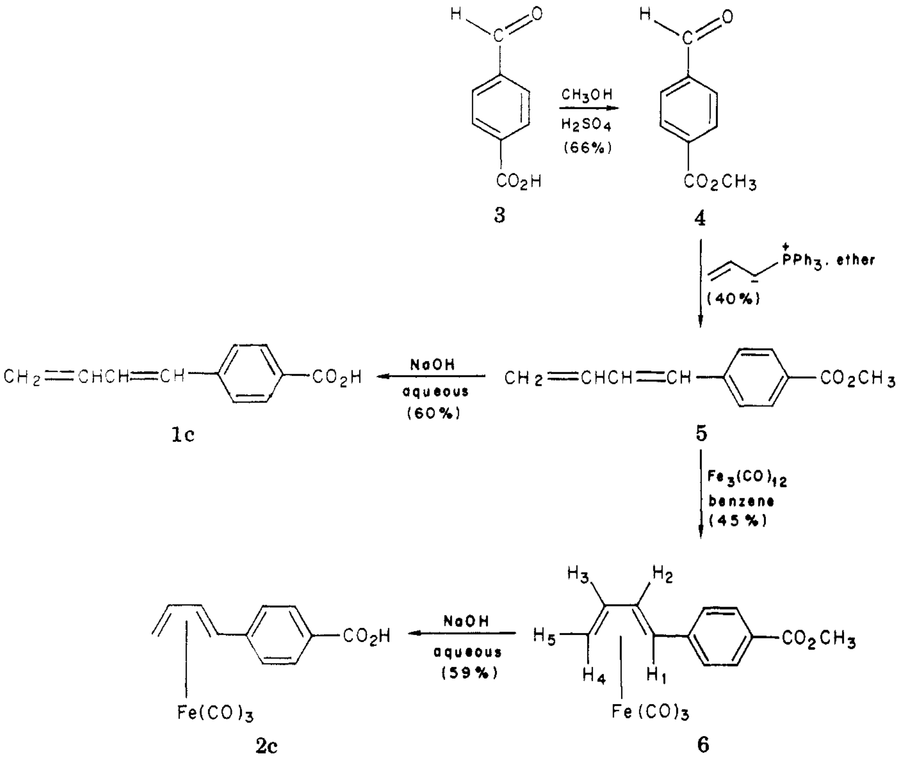
Scheme I[a]



[a] Yields are given in parentheses on arrows.

Experimental Section

General Methods. Capillary melting points were taken with a Thomas-Hoover Unimelt apparatus and are uncorrected. The infrared (IR) spectra were recorded on a Perkin-Elmer Model 257 grating spectrophotometer, calibrated with the 1944- and the 1601-cm^{-1} bands of polystyrene. Nuclear magnetic resonance (NMR) spectra were determined with a Varian A-60 or a Perkin-Elmer R12B spectrometer; the chemical shifts are expressed in parts per million (δ) downfield from tetramethylsilane used as an internal standard; coupling constants (J) are accurate to ±0.50 Hz. Analyses were performed by Schwartzkopf Microanalytical Laboratory. Column chromatography was carried out by using the "dry column" method of Loev[11] on silica gel (approximately grade III, 60–200 mesh). Commercial benzoic acid was purified by repeated recrystallization.

***p*-(Carbomethoxy)benzaldehyde (4).** *p*-Carboxybenzaldehyde (50 g, 0.33 mol) in 125 mL of 1,2-dichloroethane was mixed with 5 mL of concentrated H_2SO_4 and 30 mL of absolute methanol and stirred at reflux for 23 h. When the mixture cooled, the organic layer was separated, gravity filtered, and then washed successively with 1 L of saturated aqueous sodium bicarbonate and 1 L of 0.1 N HCl.[12] The resulting solution was then dried over anhydrous sodium sulfate and filtered, and the solvent was removed under reduced pressure. The yellow-white crystals which resulted were recrystallized from ligroin (bp 90–120 °C): white needles; 32.5 g (66%); mp 59–60 °C (lit.[13] mp 61–62 °C).

1-[*p*-(Carbomethoxy)phenyl]-1,3-butadiene (5). Into a dried 1-L three-necked, round-bottomed flask (equipped with a reflux condenser, a 250-mL addition funnel, and a rubber septum and under a nitrogen atmosphere) were placed 19.3 g (0.050 mol) allyltriphenylphosphonium bromide[14] and 300 mL of anhydrous diethyl ether. The phosphonium salt was vigorously stirred while 25 mL of 2.28 N phenyllithium was added with a syringe through the septum. The solution became deep red and was stirred overnight. *p*-(Carbomethoxy)benzaldehyde (4; 8.15 g, 0.050 mol) in 200 mL of anhydrous diethyl ether was added over a 20-min period through the addition funnel. The yellow betaine formed immediately on addition of 4. Heat was applied, and the mixture was kept at reflux for 48 h; vigorous stirring and a nitrogen atmosphere were maintained throughout the reflux period. The solution then was cooled and filtered by suction. The solid was washed with ether, and the combined ether filtrates were washed first with 1 L of 0.1 N HCl and then with 1 L of saturated aqueous sodium bicarbonate. The ether solution was dried over anhydrous sodium sulfate, filtered, and concentrated to 10 mL. The residue was absorbed onto a small amount of silica gel, dried, and placed on top of a column containing 190 g of silica gel. Elution of the column was accomplished with various solvents. Elution with ligroin (bp 60–90 °C) was carried out until no biphenyl remained. Benzene–ligroin (50/50) was then used, and elution proceeded with the collection of 200-mL fractions. Fractions 2–5 contained 3.86 g (40%) of 5: clear liquid; IR (CCl_4) 1730 (C=O), 1613, 1490, 1284, 1110 cm^{-1}; NMR ($CDCl_3$) δ 8.10–7.15 [q, 4, Ar H, consisting of 8.10–7.85 (d, 2, J = 7 Hz) and 7.40–7.15 (d, 2, J = 7 Hz)], 7.12–6.20 (m, 3-HC=CHCH=), 5.55–5.10 (m, 2, =CH_2), and 3.87 (s, 3, OCH_3). Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.59; H, 6.38. Found: C, 76.59; H, 6.55.

Further elution with benzene–ligroin (50/50) yielded unreacted 4. Elution with benzene removed small amounts of triphenylphosphine oxide. Compound 5 cannot be stored for long periods since it polymerizes into a hard white solid.

[1-[*p*-(Carbomethoxy)phenyl]-1,3-butadiene]tricarbonyliron (6). A mixture of 5 (3.0 g, 0.016 mol), dodecacarbonyltriiron (containing 5–10% methanol;[15] 9.0 g, 0.020 mol), and dry benzene (450 mL) were placed in a 1-L round-bottomed flask, and the mixture was stirred and heated at reflux for 24 h under a nitrogen atmosphere. Upon cooling, the mixture was filtered by using suction, and the filtrate was concentrated to approximately 30 mL; the residue was absorbed onto enough silica gel and, after drying, was placed on top of a column containing 190 g of silica gel. Elution with ligroin separated a green band which was removed with the ligroin. Elution with benzene separated a yellow band which was removed with the benzene solvent and collected. Removal of the benzene solvent yielded a yellow

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[11] B. Loev and M. M. Goodman, *Chem. Ind.* (*London*), 2026 (1967).

[12] The mixture must be washed well with the acid in order to hydrolyze any acetal which forms during esterification. Incomplete hydrolysis is noted by failure of the crude product to dissolve in hot ligroin (bp 90–120 °C).

[13] M. Pomerantz, *J. Am. Chem. Soc.*, 88, 5349 (1966).

[14] G. Wittig and U. Schollkopf, *Chem. Ber.*, 87, 1318 (1954).

[15] Purchased from Alfa Inorganics.

oil. The oil was taken up in ether, filtered, and concentrated; removal of the ether yielded a yellow powder: 1.5 g (46%); mp 99-100 °C. Heating this solid to 100 °C in vacuo (a vacuum sublimation apparatus serves the purpose) removed volatile impurities; the recovered solid had a melting point of 106-107 °C and was pure: IR ($CHCl_3$) 2061, 1985 ($C\equiv O$), 1720 ($C=O$), 1610, 1490, 1290 cm^{-1}; NMR ($CDCl_3$) δ 7.90-6.75 [q, 4, ArH, consisting of 7.90-7.65 (d, 2, J = 7 Hz) and 7.00-6.75 (d, 2, J = 7 Hz)], 5.80-5.20 (m, 2, H_2 and H_3 complexed vinyl protons), 4.10-3.90 (d, 1, J = 8 Hz, H_1 complexed vinyl proton), 3.85 (s, 3, OCH_3), 2.15-1.93 (m, 1, H_5 complexed vinyl proton), 0.93-0.70 (dd, 1, J = 2, 5 Hz, H_4 complexed vinyl proton). Anal. Calcd for $C_{15}H_{12}O_5Fe$: C, 54.91; H, 3.66. Found: C, 54.85; H, 3.69.

p-(1,3-Butadienyl)benzoic Acid (1c). Compound 5 (2.0 g, 0.011 mol) and 25 mL of 20% NaOH were placed in a 100-mL round-bottomed flask. The mixture was refluxed for 12 h. Upon cooling, the mixture was gravity filtered, and the filtrate was acidified with dilute sulfuric acid; fluffy white crystals precipitated. These crystals were collected by suction filtration and recrystallized from ethanol-water: 1.15 g (60%); mp 126-127 °C; IR (KBr) 1750 ($C=O$), 1600, 1420, 1390 cm^{-1}. Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.83; H, 5.79. Found: C, 75.67; H, 5.51.

p-[(π-1,3-Butadiene)tricarbonyliron]benzoic Acid (2c). Compound 6 (2.0 g, 6.1 mmol) and 25 mL of 20% NaOH were added to a 100-mL round-bottomed flask, and the mixture was heated at reflux for 12 h. Upon cooling, the solution was gravity filtered, and the yellow filtrate was acidified with dilute sulfuric acid. The yellow-green crystals which precipitated were collected by suction filtration. Recrystallization from ethanol-water produced **2c**: 1.13 g (59%); mp 170-175 °C dec; IR (KBr) 2990, 2040, 1950 ($C\equiv O$), 1750 ($C=O$), 1600, 1420, 1390 cm^{-1}. Anal. Calcd for $C_{14}H_{10}O_5Fe$: C, 53.52; H, 3.21. Found: C, 53.93; H, 2.98.

pK_a Measurements.[17] All pK_a measurements were carried out in 80% ethanol-water (80/20 by volume) by titrimetric methods at 25 ± 1 °C. Solvents were degassed before titration and stirred with a stream of nitrogen during titration. A Corning Model 12 pH meter was used equipped with a Beckman glass electrode. Standardization was carried out by using an aqueous ethanol buffer.[16]

Aqueous ethanol solutions of acids **1c** and **2c** and benzoic acid were prepared; concentrations were standardized to 0.1 N. These solutions were titrated with standardized 0.1 N NaOH. During the titration, for each increment of base added sufficient ethanol was added to maintain the 80% composition, and pH values were obtained. Calculations were carried out as exemplified by Albert and Serjeant[5] except no activity corrections were made. The average deviation within any titration varied from 0.03 to 0.09 pH units; two titrations were done for each of the acids.

Registry No. 1c, 79201-19-7; 2c, 79215-47-7; 3, 619-66-9; 4, 1571-08-0; 5, 79201-20-0; 6, 79201-10-8; $Fe_3(CO)_{12}$, 17685-52-8.

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[16] R. G. Bates, "Determination of pH", Wiley, New York, 1964, p 227.

[17] D. Stierle, E. R. Biehl, P. C. Reeves, *J. Organomet. Chem.*, **72**, 221 (1974).

Regioselective γ-Elimination of Sulfones under Michael Reaction Conditions

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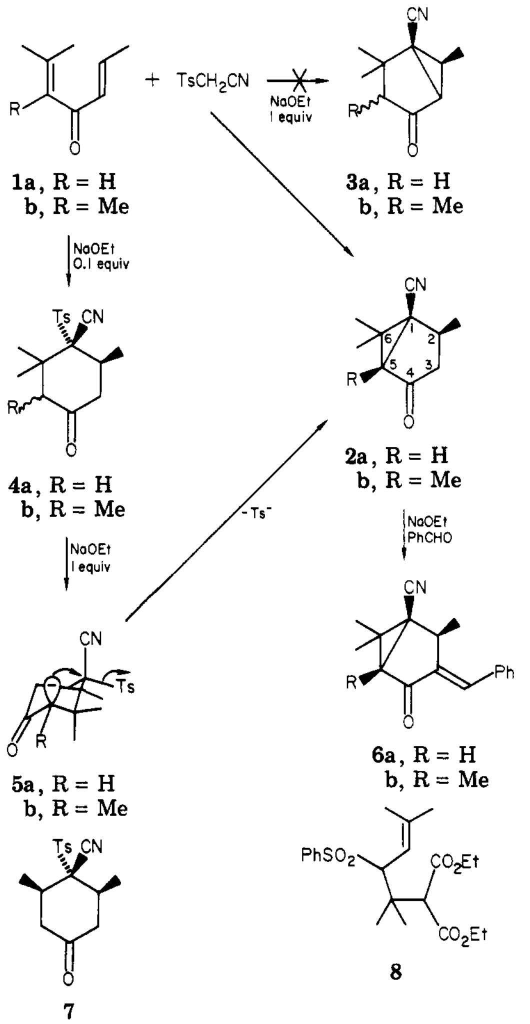
The double Michael reaction of [(4-methylbenzene)-sulfonyl)]acetonitrile with 2-methyl-2,5-heptadien-4-one (**1a**) gives[1] a bicyclic nitrile. Of the alternative structures **2a** and **3a**, we originally[1] favored **3a**. In fact, the correct structure is **2a** as shown in Scheme I.

Scheme I



The Michael reaction product **4a** is obtained when 0.1 molar equiv of sodium ethoxide is employed and is probably an intermediate in the formation of **2a**. Treatment of **4a** with 1 equiv of base leads to the same nitrile **2a** as is obtained by the one-step procedure.

The original assignment of structure **3a** was motivated by two kinetic considerations: either (i) the protons at C_3 are more accessible for enolization or (ii) the transition state leading to **3a** is less crowded. Evidently i is not a significant factor, since the methyl substituted homologue **1b** cyclizes equally regioselectively, to provide bicyclic nitrile **2b**. Regarding ii, it is now clear that in this instance the well-documented[2] "*gem*-dimethyl effect" has a decisive influence on the course of the reaction.

The structure of the bicyclic nitriles (**2a,b**) was established by preparation of the benzylidene derivatives (**6a,b**) and by 360-MHz NMR spectroscopy. The cis stereochemistry at C_2 is assigned in view of the substantial deshielding of the methine proton at that position (**3a**, δ 2.50; **3b**, δ 2.44). This is attributed to either steric crowding[3] or cyclopropane anisotropy.[4-6] Mechanistic considerations

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[1] Britten-Kelly, M.; Willis, B. J.; Barton, D. H. R. *Synthesis* **1980**, 27.

[2] Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. "Conformational Analysis"; Wiley-Interscience: New York, 1965; p 191.

[3] Winstein, S.; Carter, P.; Anet, F. A. L.; Bourn, A. J. R. *J. Am. Chem. Soc.* **1965**, *87*, 5247.

[4] Poulter, C. D.; Boikess, R. S.; Braumann, J. I.; Winstein, S. *J. Am. Chem. Soc.* **1972**, *94*, 2291.

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