Experimental Section

General Procedure for the Preparation of N-Substituted 1,4-Dihydro-3(2*H*)-isoquinolinones (11–17). A mixture of 2-isocumaranone (0.05 mole) and the desired aromatic amine (0.055 mole) was heated in a steel bomb at 220–250° for 24 hr. After cooling, the reaction mixture was dissolved in ether (or chloroform), and the solution was washed with dilute hydrochloric acid, dilute sodium hydroxide, and finally water. After drying over anhydrous magnesium sulfate, the solvent was evaporated, and the residue was distilled at reduced pressure. Chromatography on Florisil, using ethyl acetate–hexane or chloroform–hexane as developing solvents, resulted in analytically pure products.

All substances gave a single spot on thin layer chromatography. Infrared and nmr spectra were consistent with the assigned structures in all cases.

General Procedure for the Preparation of N-Benzyl-N-(*o*-tolyl)-amides 1–10. A solution of N-benzyl-*o*-toluidine (0.05 mole) and triethylamine (0.05 mole) in 50 ml of ether was cooled in an ice bath, and a solution of the desired acid chloride (0.05 mole) in 50 ml of ether was added dropwise to the stirred amine solution. After being allowed to stand overnight at room temperature, the reaction mixture was poured over ice. The ethereal layer was washed with dilute hydrochloric acid, dilute sodium hydroxide, and water. After drying over anhydrous magnesium sulfate, the ether solvent was removed *in vacuo*, and the residue was distilled at reduced pressure, or crystallized from an appropriate solvent. Yields ranged from 40 to 80%.

The formamide **1** and the trifluoroacetamide **9** were prepared by refluxing N-benzyl-*o*-toluidine in formic acid and trifluoroacetic anhydride, respectively. The reaction mixtures were worked up as described above.

Deuteration of N-(*o*-Tolyl)-1,4-dihydro-3(2*H*)-isoquinolinone (12-4-d_2). A solution of sodium methoxide (4.0 g) in 35 ml of deuterium oxide was added to a solution of N-(*o*-tolyl)-1,4-dihydro-3(2*H*)-isoquinolinone (5.0 g) in 35 ml of anhydrous dimethylformamide and the mixture was stirred under nitrogen at 80° for 2.5 hr. After the reaction mixture had been cooled to 0°, 10 ml of deuterium oxide was added. The solid was filtered and washed with deuterium oxide, yield 4.1 g. Essentially complete exchange (97%) of both C-4 methylene hydrogens was indicated by the nmr spectrum. After an additional exchange, the doubly deuterated amide was purified by chromatography on Florisil (250 g). The product was eluted with 1:9 ethyl acetate–hexane and crystallized from the same ethyl acetate–hexane solvent mixture; mp 100–102°. The nmr spectrum indicated complete disappearance of the C-4 methylene signal, while the C-1 methylene signal was recorded as an AB quartet lacking the fine splitting which was observed with the nondeuterated compound.

2-(*o*-Tolyl)isoindolin-1-one (19). Phthalide (6.70 g) and *o*-toluidine (5.88 g) were heated in a steel bomb at 250° for 48 hr. The reaction mixture was dissolved in ether and extracted with 1 *N* hydrochloric acid and then shaken twice for 0.5 hr with 1 *N* sodium hydroxide in order to remove unreacted phthalide. The ethereal solution was washed with water and dried over anhydrous magnesium sulfate, and the solvent was evaporated *in vacuo*, yield 7.2 g. The crude product was chromatographed on Florisil (250 g, ethyl acetate–hexane eluent) and recrystallized from ethyl acetate–hexane, mp 99–100°, single spot on thin layer chromatography. The nmr spectrum showed a singlet (down to a temperature of −40°) at τ 5.38 assigned to the C-3 methylene protons.

Anal. Calcd for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.64; H, 6.14; N, 6.36.

1-Benzyl-8-methyl-3,4-dihydro-2(1*H*)-quinolinone (18). Sodium hydride (1.25 g) was added to a solution of 8-methyl-3,4-dihydro-2-(1*H*)-quinolinone[25,26] (4.2 g) in 35 ml of anhydrous dimethylformamide. Dissolution of the sodium hydride was facilitated by brief warming on a steam bath. The stirred solution was cooled in an ice bath, and benzyl chloride (4.15 gm) was added dropwise during 15 min. After stirring for an additional 15 min at 0°, the reaction mixture was heated briefly on a steam bath and allowed to stand overnight at room temperature. The solvent was evaporated *in vacuo;* the residue was partitioned between water and chloroform and the organic layer dried over anhydrous magnesium sulfate. Evaporation of the chloroform solvent *in vacuo* afforded 6.5 g of an oil which showed no indication of absorption at 2.5–3 μ (N–H stretch). The product was chromatographed on Florisil (300 g) using ethyl acetate–hexane mixtures for elution. Fractions were combined on the basis of analytical thin layer chromatograms. The product (5.2 g) was distilled; bp 150° (0.1 mm), single spot on thin layer chromatography. The nmr spectrum exhibited a singlet (at room temperature and down to −40°) at τ 4.91 assigned to the N-benzyl methylene protons.

Anal. Calcd for $C_{17}H_{17}NO$: C, 81.24; H, 6.87; N, 5.57. Found: C, 81.18; H, 6.99; N, 5.53.

(25) Using the Friedel–Crafts reaction conditions described[26] led to the formation of two additional methyl isomers from which the 8-methyl compound was separated by chromatography on Fluorisil, mp 128–130° (lit.[26] mp 112°). Reduction of this product with diborane yielded 8-methyl-1,2,3,4-tetrahydroquinoline, identical in all respects with an authentic sample which was prepared by catalytic reduction of 8-methylquinoline.

(26) F. Mayer, L. van Zütphen, and H. Philipps, *Ber.*, **60**, 858 (1927).

An *ortho* Effect in the Mass Spectra of Some Carbonyl-Substituted Phenylferrocenes

Durward T. Roberts, Jr.,[1] William F. Little, and Maurice M. Bursey

Contribution from the Venable Chemical Laboratory, The University of North Carolina, Chapel Hill, North Carolina 27514. *Received April 24, 1967*

Abstract: An unusual type of mass spectral decomposition of methyl esters, loss of formaldehyde, is found in certain *ortho*-substituted ferrocenylbenzenes. The reaction is interpreted in terms of a mass spectral *ortho* effect with different geometrical requirements from those previously noted, and suggests that there may be a general class of *ortho*-effect reactions not predictable by the six-membered ring rule. Other features of the spectra of carbonyl-substituted phenylferrocenes follow patterns typical of the compound types.

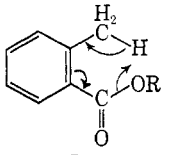
When the mass spectra of positional isomers of substituted aromatic rings are compared, there are often obvious differences between the fragmentation pattern of the *ortho* isomer and those of the *meta* and *para* isomers. Distinction between *ortho* isomers and the others may, in these cases, be made on the basis of the mass spectrum. Previous observations of this useful[2–4] type of rearrangement have been made in the

(1) DuPont Teaching Fellow, 1966–1967; Enka Summer Fellow, 1966.

(2) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964, p 194.

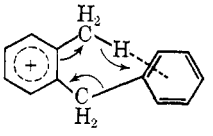
(3) F. W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, Inc., New York, N. Y., 1966: (a) p 133; (b) p 200.

spectra of aromatic acids and esters,[5-10] amides,[11] benzyl alcohols,[12] aryl sulfones,[13] nitroaromatics,[14] diarylmethanes,[15] and diaryl ethers.[16] For the most part, the structural requirements for the special *ortho*-isomer reaction appear to be explained by the assumption of a six-membered ring, *e.g.*, I, in the transition state. The classical examples[5-9,11-14] are readily explained on this basis; a five-membered ring was in-



I

voked to explain certain ions in the mass spectra of esters of pyrrolecarboxylic acids[10] and to illustrate the loss of water from salicylaldehyde.[3b] Closer examination of the spectra of diarylmethanes has led Meyerson and his co-workers to suggest[14,15] that for this case prior formation of a σ or π complex (II) precedes the decomposition. The absence of an easily detectable isotope effect would require that the C–H bond does not rupture during the rate-determining step; they suggest that the C–C bond ruptures in the rate-determining step



II

and that the full transfer of H is made as the transition state collapses.

The thought that there might be a whole class of *ortho* effects occasioned by steric factors favoring complexes with a second ring suggested a search for these examples. As a test for favorable geometry, we have used nmr data for determination of the environment of protons which might be candidates for transfer. In particular, protons whose resonances indicate that they lie within the shielding volume of an adjacent aromatic system were considered worthy of further study.

The methyl protons of *o*-ferrocenylacetophenone resonate at τ 7.91; those of the *meta* and *para* isomers resonate at τ 7.41 and 7.43, respectively. This shift is similar to that between the methyl protons of methyl *o*-ferrocenylbenzoate (τ 6.28) and those of methyl *m*-ferrocenylbenzoate (τ 5.92). The upfield shift in these and other *ortho* isomers (see Experimental Section) is an example of the effect of anisotropy of the metallocene nucleus: in both cases the methyl group rides over the top of the cyclopentadienyl ring more than to its side, and therefore is in the shielding volume associated with the metallocene nucleus.[17,18] This can be explained if the electron-rich cyclopentadienyl ring is assumed to force the electron-rich oxygen of the carbonyl group away from the ferrocene; the methyl groups would be brought into the vicinity of the metallocene system.

Several reports of the fragmentation patterns of ferrocene derivatives were available for comparison with the model systems chosen. After an early examination of the mass spectra of ferrocene[19,20] and other sandwich compounds,[19] only a few papers have discussed characteristic details of the spectra of substituted ferrocenes. At first, low-voltage mass spectrometry was suggested as a method of analysis for these compounds,[21] and later studies have been concerned with the correlation of fragmentation patterns with structure, both of compounds containing one ferrocene moiety[22-24] and of compounds containing two units.[25,26] In addition, ion–molecule reactions producing small amounts of species containing more than one iron atom and more than two cyclopentadienyl units have also been reported.[27]

Mass Spectra of Ferrocenylbenzoate Esters. On inspection of the spectra of methyl ferrocenylbenzoates (Table I) and of methyl ferrocenylphenylacetates (Table II), the larger number and intensities of fragment ions from the *ortho* isomers are at once apparent. The most abundant ions in the spectra are the molecular ion and those arising from the loss of the unsubstituted cyclopentadienyl ring and α cleavage at the carbonyl group; there are also a number of "metastable ions" of significant intensity.

Table I. Principal Ions in the Mass Spectra of Methyl Ferrocenylbenzoates[a]

	—Rel inten, %—			—Rel inten, %—	
m/e	*o*	*m*	*m/e*	*o*	*m*
320	100	100	144.5	3	12
289	5	2	141	20	5
261	1	5	140	6	19
255	60	...	139	19	22
225	43	...	121	5	6
197	19	...	115	8	3
168	1	7	56	15	6

[a] Ions containing minor isotopes are not recorded here.

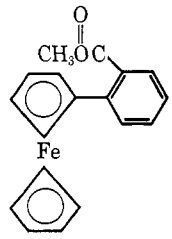
In the mass spectrum of methyl *o*-ferrocenylbenzoate (III) there is a loss of the unsubstituted cyclopentadienyl ring, giving an intense ion at *m/e* 255, followed by a loss of 30 mass units. The sequence 320 → 255 → 225 is confirmed by the appearance of "metastable ions" at *m/e* 203.2 (320 → 255) and 198.5 (255 → 225). If the

(4) G. Spiteller, "Massenspektrometrische Strukturanalyse organischer Verbindungen," Verlag Chemie, Weinheim, 1966, p 75.
(5) F. W. McLafferty and R. S. Gohlke, *Anal. Chem.*, **31**, 2076 (1959).
(6) E. M. Emery, *ibid.*, **32**, 1495 (1960).
(7) T. Aczel and H. E. Lumpkin, *ibid.*, **33**, 386 (1961).
(8) K. Biemann, *Angew. Chem.*, **74**, 102 (1962).
(9) T. Aczel and H. E. Lumpkin, *Anal. Chem.*, **34**, 33 (1962).
(10) H. Budzikiewicz, C. Djerassi, A. H. Jackson, G. W. Kenner, D. J. Newman, and J. M. Wilson, *J. Chem. Soc.*, 1949 (1964).
(11) G. Spiteller, *Monatsh. Chem.*, **92**, 1147 (1962).
(12) T. Aczel and H. E. Lumpkin, *Anal. Chem.*, **32**, 1819 (1960).
(13) S. Meyerson, H. Drews, and E. K. Fields, *ibid.*, **36**, 1294 (1964).
(14) S. Meyerson, I. Puskas, and E. K. Fields, *J. Am. Chem. Soc.*, **88**, 4974 (1966).
(15) S. Meyerson, H. Drews, and E. K. Fields, *ibid.*, **86**, 4964 (1964).
(16) R. I. Reed and J. M. Wilson, *Chem. Ind.* (London), 1428 (1962).
(17) L. N. Mulay and M. E. Fox, *J. Am. Chem. Soc.*, **84**, 1308 (1962).
(18) L. N. Mulay and M. E. Fox, *J. Chem. Phys.*, **38**, 760 (1963).
(19) L. Friedman, A. P. Irsa, and G. Wilkinson, *J. Am. Chem. Soc.*, **77**, 3689 (1955).
(20) F. W. McLafferty, *Anal. Chem.*, **28**, 306 (1956).
(21) D. J. Clancy and I. J. Spilners, *ibid.*, **34**, 1839 (1962).
(22) R. I. Reed and F. M. Tabrizi, *Appl. Spectry.*, **7**, 124 (1963).
(23) A. Mandelbaum and M. Cais, *Tetrahedron Letters*, 3847 (1964).
(24) D. W. Slocum, R. Lewis, and G. J. Mains, *Chem. Ind.* (London), 2095 (1966).
(25) C. Cordes and K. L. Rinehart, Jr., Abstracts, 150th Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1964, p 37S.
(26) E. Egger and H. Falk, *Tetrahedron Letters*, 437 (1966).
(27) E. Schumacher and T. Taubenest, *Helv. Chim. Acta*, **47**, 1525 (1964).

Table II. Principal Ions in the Mass Spectra of Methyl Ferrocenylphenylacetates

m/e	Rel inten, %: o	m	p
334	100	100	100
303	8	...	...
275	5	18	36
269	21	...	...
239	15	...	...
237	11	...	...
211	2	5	...
209	43	1	...
155	2	3	6
154	6	3	6
153	43	8	6
152	20	8	1
137.5	1	4	3
121	10	10	15
56	10	7	4

trideuteriomethyl ester is examined, the *m/e* 255 ion is shifted to *m/e* 258, and the *m/e* 225 ion is shifted to *m/e* 226. This observation may be explained by invoking a loss of CH_2O (or CD_2O, in the deuterated compound) from the methoxy group with transfer of a hydrogen to the charge-retaining fragment by some sort of cyclic mechanism. At least part of the *m/e* 225 ion is formed from the *m/e* 255 ion by this process, as the "metastable ion" at 198.5 indicates, rather than by loss of 95 units from the molecular ion. This loss of formaldehyde from methyl esters is an infrequently observed fragmentation pattern, occurring as a minor secondary process in which the primary step is centered in another functional group, and exemplified by the 194 → 163 → 133 sequence in dimethyl phthalate.[27a] The typical



III

fragmentations of such compounds are usually α cleavage[28] and, if possible, those produced by a McLafferty rearrangement[29] of the carboxylate portion.[30] Loss of formaldehyde by a cyclic mechanism is observed in the fragmentation of methyl methanesulfonate through transfer of a hydrogen with cleavage of the sulfur–oxygen bond.[31] There are also minor routes for decomposition of butyl propionate[32] and butyl acetate,[33] and for several neopentyl esters[34] by loss of CH_2O.

(27a) Note Added in Proof. See also the decomposition of 1,2-glycol diesters: S. Sasaki, H. Abe, Y. Itagaki, and K. Nakanishi, *Tetrahedron Letters*, 2357 (1967).

(28) Reference 3, p 112.

(29) F. W. McLafferty, *Anal. Chem.*, **31**, 82 (1959).

(30) R. Ryhage and E. Stenhagen, "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, p 399.

(31) W. E. Truce, R. W. Campbell, and G. D. Madding, *J. Org. Chem.*, **32**, 308 (1967).

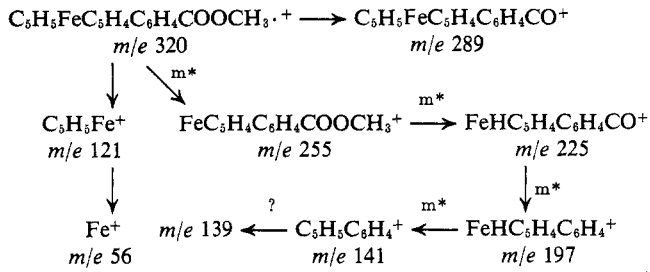
(32) C. Djerassi and C. Fenselau, *J. Am. Chem. Soc.*, **87**, 5756 (1965).

(33) D. R. Black, W. H. McFadden, and J. W. Corse, *J. Phys. Chem.*, **68**, 1237 (1964).

(34) W. H. McFadden, K. L. Stevens, S. Meyerson, G. J. Karabatsos, and C. E. Orzech, Jr., **69**, *ibid.*, 1742 (1965).

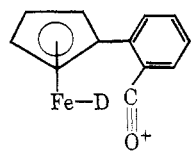
Other ions in the spectrum of methyl *o*-ferrocenylbenzoate (Scheme I) indicate the loss of a methoxy radi-

Scheme I[a]

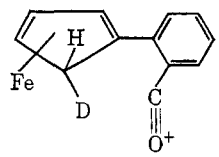


[a] Other paths for formation of ions, notably those of *m/e* 56 and 121, are not excluded in this rationalization, nor in those following.

cal from the parent ion by α cleavage, giving an ion of *m/e* 289. Additional decompositions of the *m/e* 225 ion include sequential loss of carbon monoxide and iron, giving ions of *m/e* 197 and *m/e* 141 with the appropriate "metastable ions" at *m/e* 172.5 (225 → 197) and *m/e* 100.9 (197 → 141). In the deuterated analog these ions are, as expected, shifted to *m/e* 198 and 142, respectively. There is also an ion at *m/e* 139 of unknown structure which is not shifted in the spectrum of the deuteriated compound; since deuterium is preferentially lost either as HD from *m/e* 142 or as FeHD from *m/e* 198, the transferred hydrogen atom in the *m/e* 198 ion must retain its identity. Possible structures for the *m/e* 198 ion meeting this criterion are IV and V, but distinction between them (and other structures of like symmetry) cannot be made on a firm basis. Although transfer of alkyl and acyl groups to metal atoms is documented in



IV



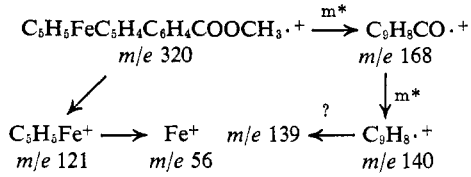
V

the mass spectra of π-bonded organometallics,[23,35] no evidence for a Fe–H bond could be secured in the present case; there were no traces of FeH^+ or species of similar utility in the spectrum. On the other hand, if the sequence 198 → 142 → 139 exists, then *m/e* 198 cannot have structure V, since the deuterium would be equivalent to another hydrogen and a shift of 50% of the intensity of *m/e* 139 to 140 would be expected. The simplest explanations consistent with the facts are that *m/e* 139 is formed directly from *m/e* 198, or else that considerable alteration of the structure of the hydrocarbon structure, in such a fashion that the D retains its identity in *m/e* 142, has occurred.

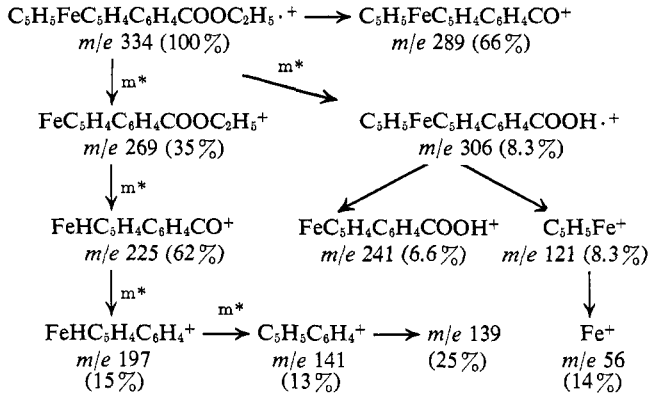
Examination of the spectrum of methyl *m*-ferrocenylbenzoate indicates that the behavior of the *ortho* isomer is peculiar to that substitution pattern. Remarkably, a "metastable ion" at *m/e* 88.2 indicates that the transition (320 → 168) occurs in one step in the *meta* isomer; this would correspond to the simultaneous loss of methoxy and cyclopentadienyliron. If a rearrangement is involved, it seems to have rather loose steric requirements. Otherwise, a fragmentation pattern typical (Scheme II) of ferrocenes is found; the more prominent fragment ions of various carbonyl-

(35) N. Maoz, A. Mandelbaum, and M. Cais, *Tetrahedron Letters*, 2087 (1965).

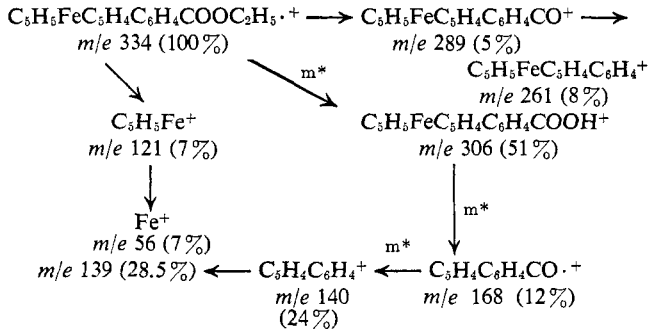
Scheme II



Scheme III



Scheme IV

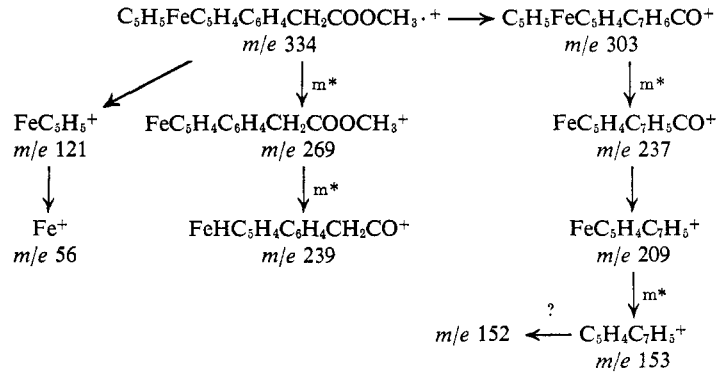


pulsion of acetaldehyde[37] and transfer of hydrogen or whether a methyl group would be transferred with loss of formaldehyde. The scheme indicated by the mass spectrum (Scheme III) shows that hydrogen transfer is preferred to the exclusion of methyl transfer. The fragmentation is quite similar to that of the methyl compound, except for an expected loss of ethylene from the molecular ion and from the *m/e* 269 fragment and a loss of the ethoxy radical by α cleavage of the molecular ion.

In the *meta* ethyl ester, there is a loss of ethylene from the molecular ion, producing *m/e* 306 and a "metastable ion" at *m/e* 280.1. It is this ion which undergoes the unusual loss analogous to that noted for the *m*-methyl ester: simultaneous loss of hydroxyl, iron, and cyclopentadienyl fragments is indicated by a "metastable ion" at *m/e* 92.5 (306 → 168). The other decompositions of the compound given in Scheme IV are typical; again, there is a doubly charged ion at *m/e* 144.5 (8%), corresponding to the doubly charged substituted benzoyl ion.

Spectra of Ferrocenylphenylacetate Esters. A second series of esters, methyl *o*-, *m*-, and *p*-ferrocenylphenylacetates, was prepared to examine the scope of the *ortho* effect further. The operation of the *ortho* effect in these esters is again apparent. In the spectrum of methyl *o*-ferrocenylphenylacetate (Table II, Scheme V), there is first a loss of the unsubstituted cyclopentadienyl ring to give an ion of *m/e* 269. This decomposes further by loss of 30 mass units. In the spectrum of the trideuteriomethyl ester these are shifted to *m/e* 272 and 240, respectively; again, this suggests the loss of formaldehyde from the methoxy group. These peaks are less intense in the phenylacetate spectrum than the corresponding ones in the benzoate spectrum. It would

Scheme V



ferrocenes[23] seem to be less prominent in these examples where the carbonyl group is attached to the benzene ring. For example, the *m/e* 121 and *m/e* 56 ions are not as intense in phenylferrocenes as they are in previously reported examples.[23,24] Presumably this reflects the greater ability of the aryl-substituted cyclopentadienyl ring to compete for the charge in the cleavage of the cyclopentadienyl–iron bond.[36] There is also an intense doubly charged ion (12.5%) at 144.5, corresponding to a substituted benzoyl ion.

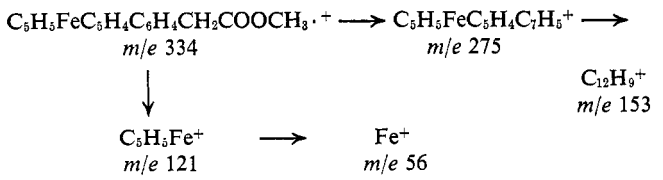
The scope of this new example of an *ortho* effect was examined in several ways. First, the ethyl ester of *o*-ferrocenylbenzoic acid was prepared to determine whether the rearrangement would correspond to exappear that the rearrangement is slightly less favorable because of steric factors in the former case.

Other evidence of interaction of the *ortho* substituent with the ferrocene system is obvious from further examination of the spectrum of this compound, summarized in Scheme V. After loss of a methoxy radical from the molecular ion, the ion loses C_5H_6, giving *m/e* 237 and a "metastable ion" at *m/e* 184.9 (303 → 237). Sequential loss of CO and Fe produces ions of *m/e* 209 and 153, respectively, with a "metastable ion" of *m/e* 112.0 connecting these latter two ions. The origin and structural characteristics of the ion of *m/e* 152 are uncertain. None of the ions below *m/e* 239 are shifted in the spectrum of the deuterium analog.

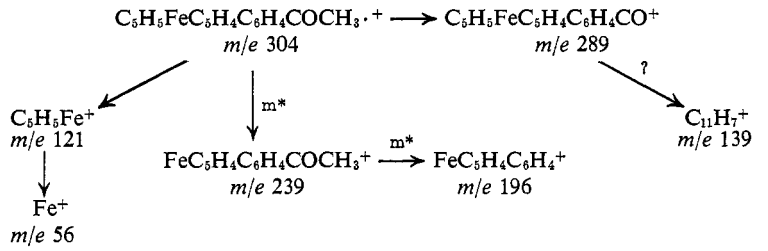
(36) *Cf.* F. W. McLafferty, ref 30, p 309.

(37) Compare the loss of acetaldehyde from *sec*-butyl acetate.[33]

Scheme VI



Scheme VII



In the spectra of the *meta* and *para* isomers of the phenylacetate ester, there is no simultaneous loss of cyclopentadienyl, iron, and alkoxy fragments, as was the case with the *meta* benzoate. The fragmentation (Scheme VI) is quite straightforward. The peak at *m/e* 275 results from the loss of the methoxycarbonyl group, and there is a doubly charged species at *m/e* 137.5 of similar composition. The singly charged ion may well have undergone ring expansion to a substituted tropylium ion.[38] The *m/e* 121 and *m/e* 56 ions are of low intensity as was noted in connection with the *meta* benzoate ester.

Spectra of Ferrocenylacetophenones. A third series of compounds, the ferrocenylacetophenones (Table III), for study of this new rearrangement is suggested by

Table III. Principal Ions in the Mass Spectra of Ferrocenylacetophenones

	Rel inten, %		
m/e	*o*	*m*	*p*
304	76	100	100
289	7	...	...
261	...	16	19
239	100	...	...
203	1	8	2
196	17	1	...
165	7	4.5	...
153	9	4	2
144.5	6	13	11
139	10	19	7
121	3	19	10
56	10	16	7

comparison of the nmr spectra of the compounds. In the spectrum of the *ortho* ketone, however, there is no evidence of a rearrangement. The spectrum (Scheme VII) is similar to that of the *ortho* esters only in that there is a loss of the unsubstituted cyclopentadienyl ring, giving *m/e* 239 and a "metastable ion" at 187.9 (304 → 239). Further loss of acetyl produces *m/e* 196 and a "metastable" at 160.7. Ions of less intensity appear at *m/e* 289 (M − 15), 165 ($C_{13}H_9$), 153 ($C_{12}H_9$), 144.5 (M − 15^{2+}), 139 ($C_{11}H_7$), 121 (FeC_5H_5), and 56 (Fe). Deuterium labeling of the methyl group indicates that the *m/e* 165 and 153 ions probably incorporate the methyl carbon, but that partial scrambling of the methyl hydrogens occurs before hydrogen is lost from

(38) See the review by H. M. Grubb and S. Meyerson (ref 30, pp 453 and 453) for an examination of the structures which may lead to symmetrical $C_7H_7^+$ ions.

either ion; the former is shifted about equally to *m/e* 167 and 168, the latter to 154, 155, and 156. Their structures are apparently very much different from recognizable precursors. The mass spectra of the remaining isomers of the ketone are straightforward and are accommodated in Scheme VII as well. The most notable difference between these and that of the *ortho* isomer is the presence of an (M − 43) ion and the absence of the *m/e* 239 and the *m/e* 196 ions in the spectra of the *meta* and *para* isomers; this difference does not point to any demonstrable rearrangement in the *ortho* isomers, however.

Details of the *ortho* Effect. In a low-voltage study of the deuterated methyl ferrocenylbenzoate (Table IV), no isotope effect outside experimental error could be found. Data are reported in terms of the peak intensity ratio[39] for the rearranged ion and its precursor, and compared with a voltage given in terms of the fractional intensity of the *m/e* 44 ion of CO_2 relative to its intensity at 75 v.[40] The lowest value corresponds to a nominal voltage of 16 v, at which the relative intensity of the (M − 65 − 30) ion is 3% of the 75-v intensity in the ferrocenylbenzoate and 7% in the ferrocenylphenylacetate.

Table IV. Low-Voltage Intensity Ratios in the Mass Spectra of Esters

Fractional inten, CO_2	[225]/[255] $FcC_6H_4COOCH_3$	[226]/[258], $FcC_6H_4COOCD_3$
1.00	0.71	0.65
0.20	0.38	0.38
0.09	0.20	0.21
0.05	0.12	0.11
0.02	0.076	0.074
Fractional inten, CO_2	[239]/[269] $FcC_6H_4CH_2COOCH_3$	[240]/[272] $FcC_6H_4CH_2COOCD_3$
1.00	0.62	0.48
0.10	0.43	0.35
0.04	0.30	0.20
0.02	0.25	0.18

The observation for the ferrocenylbenzoate is similar to that noted by Meyerson in his study of diarylmethanes.[14,15] His conclusions for the diarylmethane system are adaptable to our system: there is a σ or π complex formed between the ferrocene unit and the transferred hydrogen before the rate-determining step, the rate-determining step may be pictured as cleavage of the C–O bond, and the hydrogen is transferred fully in a fast step after the rate-determining step.

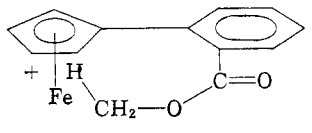
On the other hand, there is a definite isotope effect in the ferrocenylphenylacetate rearrangement which

(39) M. M. Bursey and F. W. McLafferty, *J. Am. Chem. Soc.*, **88**, 529 (1966).

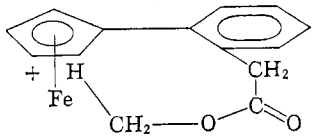
(40) M. M. Bursey and F. W. McLafferty, *ibid.*, **88**, 4484 (1966).

is relatively constant over a wide range of voltage. The data seem to be consistent with participation of the C–D bond rupture in the rate-determining step; they do not preclude, of course, formation of the complex prior to this step nor participation of the C–O bond rupture to some extent in it. It would be helpful to ascertain if further examples of this rearrangement could shed light on details of the mechanism.

Interpretation of the reaction simply in terms of the size of the transition-step ring would draw attention to the larger ring involved in these rearrangements (VI and VII) than the six-membered transition state II. *A priori*, there would have been no reason to suspect that



VI



VII

the *ortho* isomers would exhibit special behavior if the transition state required a large ring. The facts are much more easily accommodated by postulating the easy formation of a complex, rather than forcing the system into an organizational scheme which recognizes only the simple concept of the number of ring members. There are, of course, many cases[5-9,11-14] where the simple six-membered ring is sufficient to rationalize results, but *ortho* effects in which there is interaction between a substituent and an aromatic ring may well have a separate driving force, and should be distinguished from the others.

In order to search for further examples of this second type of *ortho* effect, it appears that nmr spectra may be of considerable use in screening compounds. They may be used to ascertain whether protons at a given site are properly oriented for interaction of a type that might lead to a σ or π complex which would affect the mass spectral decomposition of the molecule (*i.e.*, within the shielding cone, in the present instance). As we have illustrated with the ferrocenylacetophenones, the nmr shift is not an infallible guide, since there are certainly other structural factors which govern the energetics of ion decomposition. It would be advisable to explore both the generality of the spectral correlation noted here and the structural factors which limit its applicability.

Experimental Section

General. Melting points were determined on a Kofler hot stage and are uncorrected. Infrared spectra were recorded from samples in KBr pellets with a Perkin-Elmer Model 237 grating infrared spectrophotometer. Nmr spectra were recorded on a Varian Model A-60 spectrometer with $CDCl_3$ as solvent and tetramethylsilane as internal standard. Mass spectra were recorded on a Hitachi Perkin-Elmer Model RMU-6E mass spectrometer, at 75-v ionizing voltage and 80-μa emission current. Low-voltage spectra were recorded with 2-μa target current and 0.5-v repeller voltage. The oven was maintained at 185° and the source at 175°. The analyses were performed by Alfred Bernhardt, Mülheim (Ruhr), Germany.

Methyl *o*-Ferrocenylbenzoate. The following procedure for the formation of various *ortho*-, *meta*, and *para*-substituted phenylferrocenes was used in all similar preparations and, therefore, will be presented for this preparation alone.

A mixture of 6.5 g of methyl anthranilate (mp 24–25°; lit.[41] mp 24–25°) and 60 ml of concentrated HCl was held at 0° while 3.0 g of $NaNO_3$ was added slowly with stirring. After stirring at 0° for 1 hr, enough sulfamic acid was added to remove any remaining HNO_2. The diazonium salt was then added to 9.0 g of ferrocene (0.048 mole) in 400 ml of acetic acid and stirred overnight at room temperature under nitrogen.[42] The solution was poured into water and treated with bisulfite to reduce ferrocenium salts. The aqueous solution was extracted several times with ether. The ether fraction was washed with water, $NaHCO_3$ solution, and water, and then was evaporated. The remaining ferrocene was removed by steam distillation, and the residue was taken up in ether, which was dried over $MgSO_4$ and stripped. The residue, in hexane–benzene, was placed on a column (4 × 18 cm) of acid-washed Merck alumina. Methyl *o*-ferrocenylbenzoate was eluted with 1:1 hexane–benzene yielding 3.26 g (22.5%) of crude product. Recrystallization yielded a pure compound, mp 60.5–62° from hexane or heptane, or 74–75° from heptane (lit.[43] 74–75° from heptane) (interconvertible crystalline modifications). Chromatographic fractions containing higher phenylated products were not worked up.

Methyl *m*-ferrocenylbenzoate was prepared from 9.5 g of methyl *m*-aminobenzoate (mp 35–38°; lit.[41] mp 36–38°) (0.063 mole), yielding 2.6 g (11.8%), and was recrystallized from hexane, mp 73–74.2° (lit.[43] 70–71°).

***o*-Ferrocenylbenzoic acid** was prepared by saponification of 400 mg of methyl *o*-ferrocenylbenzoate (0.00125 mole), yielding 360 mg (95%), and recrystallized under nitrogen from methylcyclohexane, mp 128–130° (lit.[3] 128–129°).

Trideuteriomethyl *o*-Ferrocenylbenzoate. To 1.4 ml of trideuteriomethanol (Merck Sharp and Dohme of Canada) was added 112 mg of *o*-ferrocenylbenzoic acid (0.362 mmole) and 0.4 ml of $BF_3 \cdot Et_2O$.[44] The solution was held at reflux overnight, cooled, and poured into 5 ml of saturated $NaHCO_3$. The organic layer was dried with $MgSO_4$, and the ether was stripped, yielding 110.0 mg (95%). Recrystallization from hexane yielded a product of mp 60–62°.

Ethyl *o*-Ferrocenylbenzoate. To 4 ml of ethanol was added 550 mg of *o*-ferrocenylbenzoic acid (0.018 mole) and 1 ml of $BF_3 \cdot Et_2O$. The solution was held at reflux overnight and was worked up as before, yielding 505 mg (87%), recrystallized from hexane, mp 50.5–51.2°; ν^{KBr}: 3075, 1710, 1105, and 1001 cm^{-1}; nmr: τ 8.80 (t, CH_3), 5.80 (q, CH_2), 5.91 (s, C_5H_5), 5.48–5.78 (m, C_5H_4), and 2.09–2.80 (m, C_6H_4).

Anal. Calcd for $C_{18}H_{18}FeO_2$: C, 68.29; H, 5.43. Found: C, 68.39; H, 5.33.

***m*-Ferrocenylbenzoic acid** was prepared by saponification of 510 mg of methyl *m*-ferrocenylbenzoate (1.6 mmoles), yielding 485 mg (99%), and was recrystallized under nitrogen from 1:1 CH_2Cl_2–hexane, mp 169–172° (lit.[43] 166–169°).

Ethyl *m*-ferrocenylbenzoate was obtained from a previous study;[43] nmr: τ 8.62 (t, CH_3), 5.64 (q, CH_2), 6.03 (s, C_5H_5), 5.30–5.77 (m, C_5H_4), and 1.80–2.90 (m, C_6H_4).

Methyl *o*-ferrocenylphenylacetate was prepared from 7.1 g of methyl *o*-aminophenylacetate[44-46] (0.043 mole), yielding 0.8 g (5.3%), and recrystallized from hexane, yielding mp 41.1–42.1°; ν^{KBr}: 3085, 1735, 1100, and 1000 cm^{-1}; nmr: τ 6.33 (s, CH_3), 6.20 (s, CH_2), 5.80 (s, C_5H_5), 5.40–5.90 (m, C_5H_4), and 2.00–2.90 (m, C_6H_4).

Anal. Calcd for $C_{19}H_{18}FeO_2$: C, 68.29; H, 5.43. Found: C, 68.42; H, 5.32.

Methyl *m*-ferrocenylphenylacetate was prepared from 8.6 g of methyl *m*-aminophenylacetate[44,47,48] (0.053 mole), yielding 1.0 g

(41) "Dictionary of Organic Compounds," I. A. H. Heilbron, A. H. Cook, H. M. Bunbury, and D. H. Hey, Ed., Oxford University Press, London, 1965.

(42) M. Rosenblum, *J. Am. Chem. Soc.*, **81**, 4530 (1959).

(43) W. F. Little, C. N. Reilley, J. D. Johnson, K. N. Lynn, and A. P. Sanders, *ibid.*, **86**, 1376 (1964).

(44) G. Hallas, *J. Chem. Soc.*, 5770 (1965).

(45) P. W. Neber, *Chem. Ber.*, **55**, 826 (1922).

(46) Prepared from *o*-nitrophenylacetic acid (mp 140–142°) by esterifying with $BF_3 \cdot Et_2O$ in methanol and reducing the nitro group (H_2–Pt), and used directly.

(47) W. A. Jacobs and M. Heidelberger, *J. Am. Chem. Soc.*, **39**, 2418 (1917).

(48) Prepared from *m*-nitrophenylacetic acid (mp 117–119°) as in ref 46.

(6.4%), and recrystallized from hexane, mp 67–69°; ν^{KBr}: ν^{KBr} 3085, 1740 (d), 1100, and 1000 cm^{-1}; nmr: τ 6.37 (s, CH_2), 6.31 (s, CH_3), 5.98 (s, C_5H_5), 5.70–5.38 (2t, C_5H_4), and 2.56–2.93 (m, C_6H_4).

Anal. Calcd for $C_{19}H_{18}FeO_2$: C, 68.29; H, 5.43. Found: C, 68.14; H, 5.53.

Methyl *p*-Ferrocenylphenylacetate. The free acid was prepared by the previous route from 8 g of methyl *p*-aminophenylacetate[41,44,49] [bp 240–250° (17 mm)] (0.053 mole) with hydrolysis of the ester in the reaction medium yielding 3.94 g (19.4%). Recrystallization from 1:1 CH_2Cl_2–methylcyclohexane gave *p*-ferrocenylphenylacetic acid, mp 160.5–161.5°; ν^{KBr}: 3500–2500, 1710, 1100, and 1000 cm^{-1}; nmr: τ 6.40 (s, CH_2), 5.97 (s, C_5H_5), 5.70–5.32 (2t, C_5H_4), and 2.63 (ABd, C_6H_4).

Anal. Calcd for $C_{19}H_{18}FeO_2$: C, 67.52; H, 5.04. Found: C, 67.37, 67.36; H, 5.14, 5.09.

A mixture of 1.00 g of *p*-ferrocenylphenylacetic acid (3.0 mmoles), 10 ml of methanol, and then 2.3 ml of $BF_3 \cdot Et_2O$ was stirred under nitrogen at room temperature for 2 hr and poured into saturated $NaHCO_3$. The ester was filtered off, washed with water (0.75 g, 72%), dissolved in benzene, washed through a plug of alumina, and recrystallized from hexane, mp 87.0–87.7°; ν^{KBr}: 3095, 1737, 1100, and 1000 cm^{-1}; nmr: τ 6.40 (s, CH_2), 6.30 (s, CH_3), 5.97 (s, C_5H_5), 5.71–5.37 (2t, C_5H_4), and 2.70 (ABd, C_6H_4).

Anal. Calcd for $C_{19}H_{18}FeO_2$: C, 68.29; H, 5.43. Found: C, 68.27; H, 5.50.

***o*-Ferrocenylphenylacetic acid** was prepared by saponification of 200 mg of methyl *o*-ferrocenylphenylacetate (0.6 mmole) yielding 170 mg (89%); recrystallized from methylcyclohexane, mp 100–103°; ν^{KBr} 3300–2200, 1700, 1100, and 995 cm^{-1}; nmr: τ 6.14 (s, C_5H_4), 5.40–5.90 (m, C_6H_4), and 2.00–3.00 (m, C_6H_4).

Anal. Calcd for $C_{18}H_{16}FeO_2$: C, 67.52; H, 5.04. Found: C, 67.53; H, 4.89.

Trideuteriomethyl *o*-Ferrocenylphenylacetate. To 1.4 ml of trideuteriomethyl alcohol was added 102 mg of *o*-ferrocenylphenylacetic acid (0.32 mmole) and 0.4 ml of $BF_3 \cdot EtO$. The solution was stirred at room temperature for 2 hr and worked up as before, yielding 83.2 mg (77.5%); recrystallized from hexane, mp 42.44°.

(49) Prepared from *p*-nitrophenylacetic acid (mp 153–155°) as in ref 46.

***o*-Ferrocenylacetophenone** was prepared from 10 g of *o*-aminoacetophenone (Aldrich, $n^{20}D$ 1.6101) (0.329 mole) yielding 3.75 g (17.5%), and was recrystallized from hexane, mp 90–91° or 75–77° (crystalline modifications interconvertible by seeding); ν^{KBr}: 3090, 1678, 1100, and 1000 cm^{-1}; nmr: τ 7.91 (s, CH_3), 5.96 (s, C_5H_5), 5.70–5.57 (2t, C_5H_4), and 2.05–2.85 (m, C_6H_4).

Anal. Calcd for $C_{18}H_{16}FeO$: C, 71.07; H, 5.32. Found: C, 70.98; H, 5.35.[49a]

***m*-Ferrocenylacetophenone** was prepared from 5.8 g of *m*-aminoacetophenone (Aldrich) (mp 98–99°; lit.[50] 99.5°) (0.016 mole) yielding 2.03 g (14.5%) and after recrystallization from hexane melted at 73–75.5°; ν^{KBr}: 3085, 1680, 1100, and 997 cm^{-1}; nmr: τ 7.41 (s, CH_3), 5.9 (s, C_5H_5), 5.25–5.85 (m, C_6H_4), and 1.80–2.70 (m, C_6H_4).

Anal. Calcd for $C_{18}H_{16}FeO$: C, 71.07; H, 5.32. Found: C, 70.78; H, 5.37.[49a]

***p*-Ferrocenylacetophenone** was prepared from 10 g of *p*-aminoacetophenone (Aldrich) (mp 106–107°; lit.[51] mp 105–106°) (0.027 mole) yielding 4.65 g (21.5%); recrystallized from hexane, mp 174.0–174.5° (lit.[42] 176–178°).

***o*-Ferrocenylacetophenone-2,2,2-d_3.** To a mixture of 0.50 g of clean Na, 0.400 g of *o*-ferrocenylacetophenone (0.0013 mole), and 40 ml of dry peroxide-free dioxane was added 20 ml of D_2O with stirring.[52] The solution was maintained at 70° under nitrogen for 5 hr. The dioxane was removed under reduced pressure and the product isolated by extraction with ether. A single treatment gave 91% of the d_3 and 9% of the d_2 species.

Acknowledgments. We thank Mr. Laurence R. Dusold for recording many of the spectra. D. T. R. thanks E. I. du Pont de Nemours and Company, Inc., for a DuPont Teaching Fellowship and the American Enka Corporation for an Enka Summer Fellowship.

(49a) NOTE ADDED IN PROOF. Analytical data correspond to those of T. G. Traylor and J. C. Ware, *J. Am. Chem. Soc.*, **89**, 2304 (1967).

(50) H. Rupe, A. Braun, and K. von Zembruzski, *Chem. Ber.*, **34**, 3522 (1901).

(51) J. Klingel, *ibid.*, **18**, 2687 (1885).

(52) E. Lund, H. Budzikiewicz, J. M. Wilson, and C. Djerassi, *J. Am. Chem. Soc.*, **85**, 1528 (1963).

Mercury-Photosensitized Reactions of 1,4-Dienes[1]

Jerrold Meinwald and G. Warren Smith[2]

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850. *Received March 2, 1967*

Abstract: The gas-phase, mercury-photosensitized reactions of four 1,4-dienes (**1**, **9**, **15**, and **18**) have been found to yield vinylcyclopropanes (**2**, **10**, **17**, and **20**) as the major monomeric products. Accompanying these cyclization reactions, carbon skeleton rearrangements which yield isomeric 1,4-dienes, cycloadditions to form bicyclo[2.1.0]pentanes, and partial reductions to give monoolefins were detected. All of these reactions were accompanied by polymer formation. A variety of mechanisms compatible with vinylcyclopropane and rearranged diene formation are considered.

While there has long been interest in the physical aspects of mercury-photosensitized reactions,[3] the synthetic potential of these reactions has only recently been made apparent, especially as a result of the excellent work of Lemal and of Srinivasan.[4–8] Several years ago, we initiated a study of the mercury-photosensitized reactions of 1,4-dienes, in part in the hope that a route to the then unknown bicyclo[1.1.1]pentanes[9,10] might result. In fact, this particular mode of

(1) The partial support of this research by a National Science Foundation research grant and by the Chevron Research Co. is gratefully acknowledged.

(2) National Institutes of Health Predoctoral Fellow, 1963–1966.

(3) For a review of mercury-photosensitized reactions, see J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, Chapter 2; H. E. Gunning and O. P. Strausz, *Advan. Photochem.*, **1**, 209 (1963); R. J. Cvetanović, *Progr. Reaction Kinetics*, **2**, 39 (1964).

(4) D. M. Lemal and K. S. Shim, *J. Am. Chem. Soc.*, **86**, 1550 (1964).

(5) R. Srinivasan, *ibid.*, **84**, 4141 (1962).

(6) R. Srinivasan, *J. Phys. Chem.*, **67**, 1367 (1963).

(7) R. Srinivasan, *J. Am. Chem. Soc.*, **85**, 819 (1963).

(8) R. Srinivasan, *ibid.*, **86**, 3318 (1964).

(9) The first successful synthesis of bicyclo[1.1.1]pentane was reported by K. B. Wiberg, D. S. Connor, and G. M. Lampman, *Tetra-*