rected for thermal expansion of the solutions to obtain the corresponding values at 80.45°.

For the reaction of β-phenylethyltrimethylammonium bromide in a 50% H_2O–D_2O (v/v) mixture, the reaction solutions were prepared by mixing equal volumes (pipet) of H_2O and D_2O solutions.

In the reaction of β-phenylethyl bromide with sodium hydroxide in 40% aqueous dioxane, infinity determinations were not possible because of the inaccuracy of alkali determinations over a long period of time or at high temperatures (see Discussion). For this reason, and because the reaction was fairly fast, rapid mixing without a drop in temperature was necessary to ensure accurate determinations of the initial concentrations. Consequently, in almost all runs a Pyrex glass reaction vessel was used which had two chambers, both easily accessible from the mouth of the vessel. The general procedure was to weigh the alkyl bromide accurately into a semimicro weighing flask which was placed into one chamber of the vessel. The remaining procedures were carried out in a nitrogen atmosphere. By pipet, 10 ml of dioxane was added to this chamber. Into the other chamber was introduced 15 ml of standard sodium hydroxide solution, also by pipet. A rubber serum stopper was wired into the mouth of the vessel which was then placed into the constant-temperature bath. When thermal equilibrium was attained, the solutions in the two chambers were rapidly mixed by shaking the vessel from side to side and the zero time noted. The zero titer ($=a$) was determined by one of two methods: (1) the above procedure was carried out in the absence of the alkyl bromide and, after thermal equilibrium had been reached, the zero titer of the solution was determined by withdrawing a 2-ml aliquot with a calibrated hypodermic syringe, cooling in ice and titrating, under nitrogen, with 0.00990 M hydrochloric acid to pH 7, using a Beckman Model H-2 pH meter; or (2) the normality of the stock solution of sodium hydroxide was determined at room temperature and adjusted to the volume of the final solution (4% volume increase in 40% aqueous dioxane solution in going from 25 to 80°). Agreement between the two methods was excellent. The concentration of the alkyl bromide ($=b$) was determined by dividing the number of moles of alkyl bromide weighed into the flask by the final volume of the solution at 80°. Succeeding 2-ml aliquots were withdrawn, quenched in ice, and titrated under nitrogen to pH 7.

Olefin Determinations. Olefin yields were determined spectrophotometrically. Most ultraviolet absorption spectra were determined in 95% ethanol on a Perkin-Elmer Model 202 ultraviolet–visible spectrophotometer. This instrument was calibrated against a standard solution of alkaline potassium chromate[51] and found to give accurate optical densities. The extinction coefficient of olefin was also checked on a Cary Model 14 recording spectrophotometer and found to agree well with the value obtained on the Perkin-Elmer instrument. The spectra of the freshly distilled styrenes were determined under the same conditions and at the same time as were the product olefins. Beer's law was obeyed over the concentration ranges used (*ca.* 5×10^{-5} M). Molar extinction coefficients are: styrene, λ_{max} 248 $m\mu$ (ϵ 1.52×10^4);[52,53] p-chlorostyrene, λ_{max} 253 $m\mu$ (ϵ 2.06×10^4).[54]

It was established that sodium hydroxide, β-phenylethyldimethylsulfonium bromide, β-phenylethyltrimethylammonium bromide, methyl sulfide, and trimethylamine had no effect on the ultraviolet absorption of the styrenes. Dimethylaniline, formed in the reaction of phenyl-2-phenylethyldimethylammonium bromide with sodium lyoxide, absorbed strongly in the same region as styrene and these determinations were carried out in 70% ethanol, 3.24 M in HCl. In this strongly acidic solution, the absorption of the amine virtually disappeared, while that of the styrene remained unchanged except for a shift of the wavelength maximum to 249 $m\mu$. It was necessary to apply a small correction (*ca.* 3%) to account for the absorption of the protonated dimethylaniline and of the unreacted phenyl-2-phenylethyldimethylammonium bromide.

For the sulfonium salt runs, determinations were made on ampoules of reaction solution which had proceeded to completion. In the slower quaternary ammonium salt runs the determinations were made after about 50% reaction. In some of the runs partial polymerization of the styrene occurred so that the results represent maximum yields obtained from at least two separate determinations. Olefin yields were 100 ± 3%. Maximum estimated error for the determinations is 2–3%.

Acknowledgments. Support of the National Science Foundation for purchase of the Perkin-Elmer 202 spectrophotometer (IG-63-9) and support of L. J. S. by Public Health Service Fellowship No. 1-F1-GM-20,-578-01, from the Division of General Medical Sciences, is gratefully acknowledged.

---

(51) G. W. Haupt, *J. Res. Natl. Bur. Std.*, **48**, 414 (1952).

(52) Lit.[5a] λ_{max} 248 $m\mu$ (ϵ 1.38×10^4).

(53) Lit. λ_{max} 249 $m\mu$ (ϵ 1.55×10^4): O. H. Wheeler and C. B. Covarrubias, *Can. J. Chem.*, **40**, 1224 (1962).

(54) Lit.[5a] λ_{max} 253 $m\mu$ (ϵ 1.97×10^4).

Geometrical Requirements for the Loss of Aldehyde Molecules in the Mass Spectra of Ferrocenyl Esters

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. *Received June 27, 1967*

Abstract: The mass spectra of the methyl ω-ferrocenylalkanoates are compared with reference to the loss of CH_2O from the ester function. When $n = 0$, 2, or 3 in $Fc(CH_2)_nCOOCH_3$, the loss of the elements of formaldehyde occurs as a secondary process after loss of C_5H_5; when $n = 1$, 4, or 5, it does not. Another mechanism for loss of formaldehyde during decomposition of these compounds, possibly involving prior transfer of the methoxy group to the cyclopentadienyliron unit, occurs in some cases. Other routes for decomposition apparently lead to C_6H_6 and C_7H_7 units as ligands.

Recently we described an unusual *ortho* effect in the mass spectra of some ferrocenylbenzenes in which a methyl ester function on the benzene ring lost the elements of formaldehyde during a secondary decomposition.[2] We suggested that the structural features of ferrocene esters should be explored in order to determine the generality of the rearrangement. This paper examines the occurrence of this reaction in a series of esters in which the number of methylene units between the ferrocene ring and the ester function is increased from zero to five.

General Aspects of the Spectra. The significant peaks in the mass spectra of six methyl ω-ferrocenyl-

---

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

(2) D. T. Roberts, Jr., W. F. Little, and M. M. Bursey, *J. Am. Chem. Soc.*, **89**, 4917 (1967).

Table I. Principal Ions in the Mass Spectra of $C_5H_5FeC_5H_4(CH_2)_nCO_2CH_3$

	m/e (%)															
n	M⁺, %	M − OCH_3	M − C_5H_5	M − (C_5H_5 + OCH_2)	M − (C_5H_5 + $HOCH_3$)	M − (C_5H_5 + $HOCH_3$ + CO)	M − (C_5H_5 + CO)	M − (C_5H_5 + CO + CH_2O)	Misc	212	199	148	135	121	56
0	244 (100)	213 (5)	179 (2)	149 (8)	...	...	152 (47)	122 (77)	185 (4) 150 (11) 129 (8) 128 (6)	..	..	..	..	29	33
1	258 (100)	...	193 (26)	...	...	...	165 (13)	135 (30)		..	50	..	30	33	20
2	272 (100)	246 (6)	207 (43)	177 (12)	175 (14)	147 (15)	...	...	213 (6) 206 (17) 106.5 (2)	6	22	16	20	34	23
3	286 (100)	255 (13)	221 (23)	191 (14)	189 (20)	161 (23)	...	...	178 (15) 99.5 (14)	7	20	13	17	36	24
4	300 (100)	269 (8)	235 (20)	...	203 (6)	175 (32)	...	...	204 (5) 147 (4)	7	17	6	11	37	18
5	314 (100)	283 (6)	249 (12)	...	217 (6)	189 (11)	...	...	247 (8) 187 (7) 186 (6)	6	18	3	13	24	10

alkanoates are given in Table I. The spectra are in general fairly similar, with the most abundant ions corresponding to fragmentation of both the ferrocene moiety and the decompositions of the ester function. Typical fragmentation of aliphatic methyl esters,[3] which produces an (M − 31)⁺ ion and an *m/e* 74 ion, is suppressed, as if the charge were more nearly localized in the ferrocene portion of the molecule.

Each of the molecular ions loses the unsubstituted cyclopentadienyl ring, but only those compounds containing zero, two, or three methylene units lose CH_2O in a sequential step. In the case of methyl ferrocenecarboxylate (*n* = 0), which has been discussed in part previously,[4] loss of cyclopentadienyl produces an ion of *m/e* 179, which produces *m/e* 149 by loss of CH_2O, as indicated by a "metastable ion" at *m/e* 124.0. In the spectrum of the trideuteriomethyl ester, these ions are shifted to *m/e* 182 and 150, respectively. For the case in which *n* = 2, methyl β-ferrocenylpropionate, sequential loss of cyclopentadienyl and formaldehyde is indicated by "metastable peaks" at 157.6 (272 → 207) and 151.1 (207 → 177); the appropriate shifts to *m/e* 210 and 178 are observed for the corresponding fragment ions in the trideuteriomethyl ester. Finally, for the case in which *n* = 3, methyl γ-ferrocenylbutyrate, the loss of cyclopentadienyl and then formaldehyde is signaled by "metastable peaks" at *m/e* 171.0 (286 → 221) and 165.0 (221 → 191) and confirmed by the shifts in the trideuteriomethyl ester spectrum to *m/e* 224 and 192 for the appropriate ions. The latter two compounds are analogous to the methyl esters of *o*-ferrocenylbenzoic acid and *o*-ferrocenylphenylacetic acid with respect to the number of carbons separating the carbonyl group from the ferrocene nucleus; these compounds were also observed to undergo this loss of CH_2O.[2]

Another curious sequence of fragmentations observed in several spectra is the loss of CH_2O from a fragment which has previously lost the carbonyl group. In the spectrum of methyl ferrocenecarboxylate, C_5H_4CO may be lost (*m/e* 244 → 152; *m** 94.8) to yield an ion whose structure has been suggested to be I.[4] We observe a further decomposition by loss of CH_2O,

I

substantiated by a "metastable peak" at *m/e* 97.9 (152 → 122). When the trideuteriomethyl ester decomposes, the *m/e* 155 ion ($C_5H_5FeOCD_3$, according to I) loses CH_2O, CHDO, and CD_2O in the ratio of 4:7:7. In addition, half of the intensity of the common ion at *m/e* 121 is shifted to *m/e* 122 (FeC_5H_4D). Consequently it appears that partial randomization of the methoxy hydrogens and cyclopentadienyl hydrogens occurs in at least some of the ions of structure I.

Similarly, in the spectrum of methyl ferrocenylacetate, there is a sequence 258 → 193 → 165 → 135 supported by "metastable peaks" at 144.2, 141.0, and 110.3, corresponding to the loss of cyclopentadienyl, carbon monoxide, and formaldehyde in that order. In this case, the trideuteriomethyl ester shows analogous ions of *m/e* 261, 196, 168, and 136 and so the last step does not seem to occur after equilibration of the methoxy and ring hydrogens has occurred.

In the spectrum of methyl β-ferrocenylpropionate, a somewhat analogous apparent transfer of the methoxy group again occurs. The sequence 272 → 207 → 165 → 135 (*m** 157.6, 131.6, 110.3) would indicate that a loss of the elements of formaldehyde similar to the 165 → 135 sequence of the previous case occurs. In this case, the *m/e* 165 ion is formed from its predecessor by loss of C_2H_2O; there must be some particular stability of the $CH_3OFeC_6H_6^+$ ion (*m/e* 165)[5–7] since it is preferentially formed by two different routes in these two cases. In the spectrum of the trideuteriomethyl analog, the masses of the ions are fully shifted to 275, 210,

---

[3] R. Ryhage and E. Stenhagen, *Arkiv Kemi*, 13, 523 (1959).

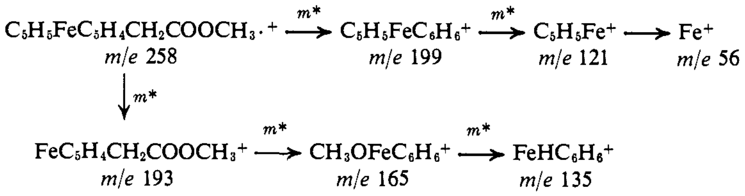
[4] A. Mandelbaum and M. Cais, *Tetrahedron Letters*, 3847 (1964).

[5] The stability of C_6H_6 as a ligand has been suggested to explain the spectrum of 1,1′-dimethylferrocene; a ring expansion similar to that encountered in the mass spectral formation of tropylium ion[6] was adduced. (a) G. W. Wilcox and R. W. Geiger, Anachem Conference, Detroit, Mich., 1963. We thank Dr. Wilcox for informing us of this observation. (b) See also H. Egger, *Monatsh.*, 97, 602 (1966).

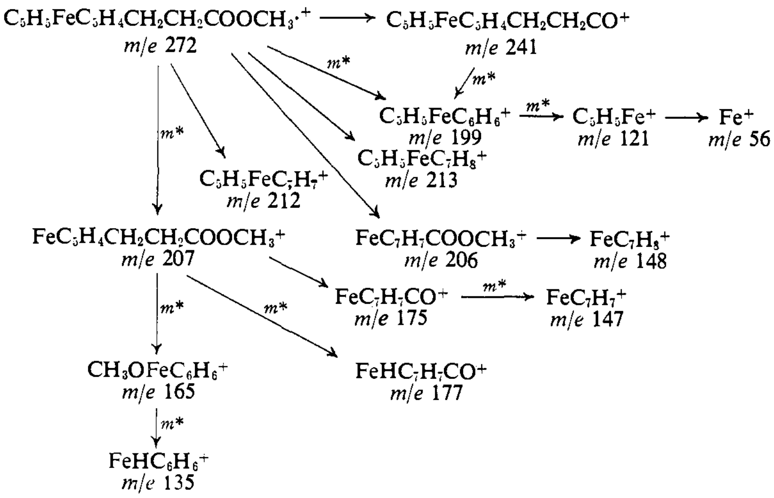
[6] H. M. Grubb and S. Meyerson ["Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, p 453] review structures leading to tropylium ions.

[7] Salts of $C_6H_6FeC_5H_5^+$ may be prepared from ferrocene, and substituted derivatives from substituted ferrocenes: A. N. Nesmeyanov, N. A. Vol'kenau, and I. N. Bolesova, *Dokl. Akad. Nauk SSSR*, 149, 615 (1963); A. N. Nesmeyanov, N. A. Vol'kenau, and L. S. Shilovtseva, *ibid.*, 160, 1327 (1965).

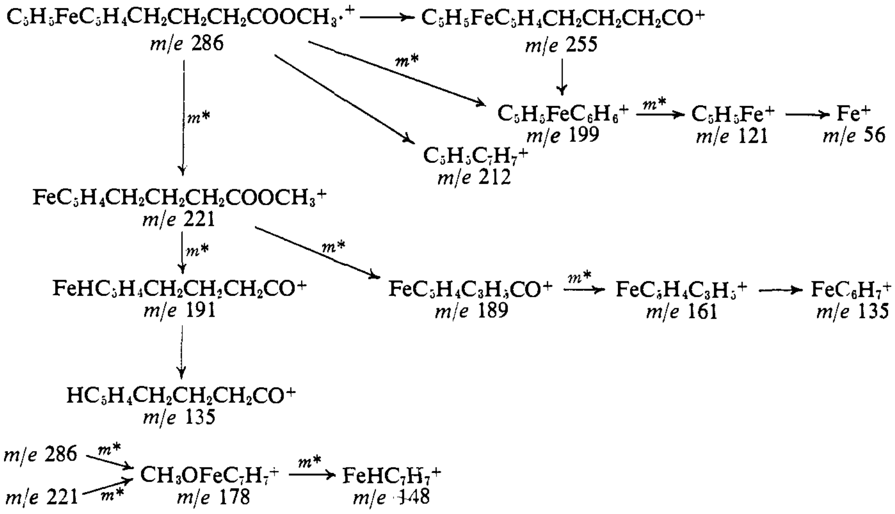
Scheme I



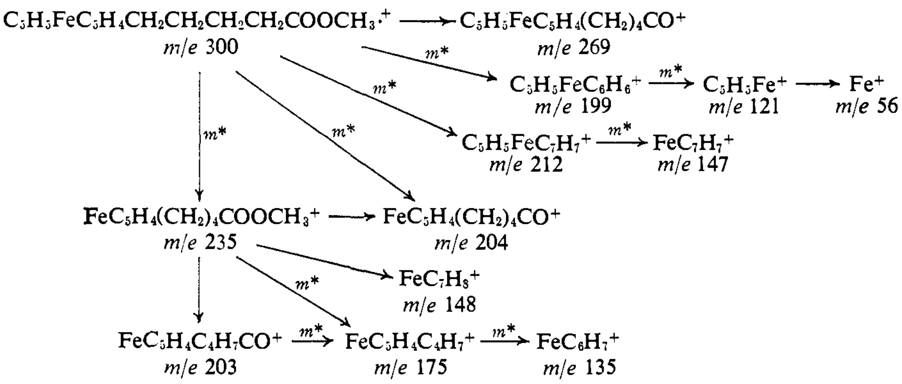
Scheme II



Scheme III



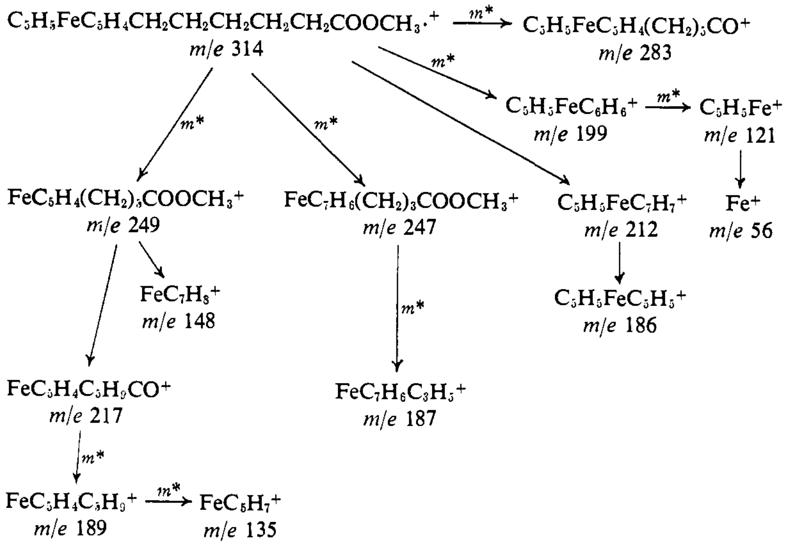
Scheme IV



168, and 136; as in the previous case, then, there is no scrambling of the hydrogens in the 168 ion. None of the other homologous esters give indication of undergoing a simple methoxy transfer in mass spectral decomposition.

Schemes I–V summarize the general features of these spectra, excepting that of methyl ferrocenecarboxylate, the general features of whose fragmentation have already been reported.[4] In addition we observe a small peak at *m/e* 150 of uncertain origin. Most of

Scheme V



the other fragmentations of the homologous series are straightforward and do not require comment. Those features which are worth elaboration are as follows: the spectrum of the ferrocenylacetate, which is straightforward, is given in Scheme I. Scheme II presents a rationale of the decomposition of the ferrocenylpropionate ester, which apparently includes a loss of CH_3OH from *m/e* 207, followed by the loss of carbon monoxide to yield $FeC_7H_7^+$ (m^* 123.5 for 175 → 147), of uncertain but intriguing structure,[8] and also the intermediacy of $C_5H_5FeC_6H_6^+$ in the sequences 272 → 199 → 121 (m^* 145.5, 73.6) and 241 → 199 → 121 (m^* 164.2, 73.6), which again suggest some energetically favorable structure for C_6H_6 as a ligand. The formation of *m/e* 212 by the elimination of $C_2H_4O_2$ from the molecular ion also is exceptional. The formation of *m/e* 206 might be due to the loss of C_5H_6 from the molecular ion. The hydrogen must come from the side chain, but not from the ester portion (the peak shifts to 209 in the trideuteriomethyl ester). The *m/e* 148 ion shows considerable randomization of methoxy hydrogens in the labeled ester; it is shifted about equally to *m/e* 149 and 150.

Many of the features of the spectrum of methyl γ-ferrocenylbutyrate (Scheme III) are similar to those of the preceding spectrum; there is again evidence for the C_6H_6 and C_7H_7 ligands, as before. The *m/e* 178 peak is related by "metastable peaks" at 143.2 and 110.9 to the $(M - C_5H_5)^+$ ion and the molecular ion and by a "metastable peak" at 123.1 to 148. In the deuterated analog, the 178 peak appears at 181 and the peak at 148 is shifted equally to 149 and 150. These observations suggest a pattern involving sequential and/or concomitant loss of C_5H_5 and C_2H_3O, so that a methoxy group is transferred to iron in $C_7H_7FeOCH_3^+$; this then loses formaldehyde, but once again, as in the ferrocenecarboxylate example, the hydrogens have been partially scrambled. Finally, a shift of 30% of the intensity of the *m/e* 135 ion to *m/e* 136 might suggest that part of this ion is formed by loss of Fe from *m/e* 191 and part by loss of C_2H_2 from *m/e* 161.

The spectra of the δ-ferrocenylvalerate and ϵ-ferrocenylcaproate (Schemes IV and V) esters indicate the stability of the C_6H_6 and C_7H_7 ligands once again. They also appear to form *m/e* 135 ($FeC_6H_7^+$) by loss of olefin (C_3H_4 and C_4H_8, respectively) from perhaps unexpected precursors. Otherwise, the patterns for decomposition seem well established.

The spectra of the ethyl esters are summarized in Schemes VI–XI and may in general be explained on the basis of the preceding discussion and the recollection that a typical fragmentation of ethyl esters is loss of ethylene to generate an ion with properties similar to that of the corresponding carboxylic acid molecular ion. The spectrum of ethyl ferrocenecarboxylate (Scheme VI) suggests neither a transfer of the ethoxy group to iron nor loss of cyclopentadienyl, so that no aldehyde is lost in decomposition. The favored processes have in general been previously described in terms of the ferrocenecarboxylic acid molecular ion.[4]

Ethyl ferrocenylacetate (Scheme VII) decomposes as might be expected on electron impact. Formation of *m/e* 135 from *m/e* 179 is indicated by a "metastable ion" at *m/e* 102.8. Since decomposition of carboxylic acids by decarboxylation is not the expected mode of fragmentation in general, it may be possible that some interaction between the iron and the carboxyl hydrogen promotes this cleavage. The C_6H_6 ligand appears again in the *m/e* 199 ion.

The spectra of ethyl β-ferrocenylpropionate and ethyl γ-ferrocenylbutyrate (Schemes VIII and IX) show sequential loss of cyclopentadienyl and acetaldehyde from the molecular ions (286 → 221 → 177, m^* 170.7 and 141.8; and 300 → 235 → 191, m^* 184.0 and 155.1, respectively), in exact analogy to the ethyl esters of *o*-ferrocenylbenzoic acid and *o*-ferrocenylphenylacetic acid.[2] Numerous ions in the spectra seem to contain the C_6H_6 and C_7H_7 ligands. The butyrate spectrum contains an ion of *m/e* 192, analogous to the *m/e* 178 ion of the methyl ester, decomposing by loss of acetaldehyde to *m/e* 148.

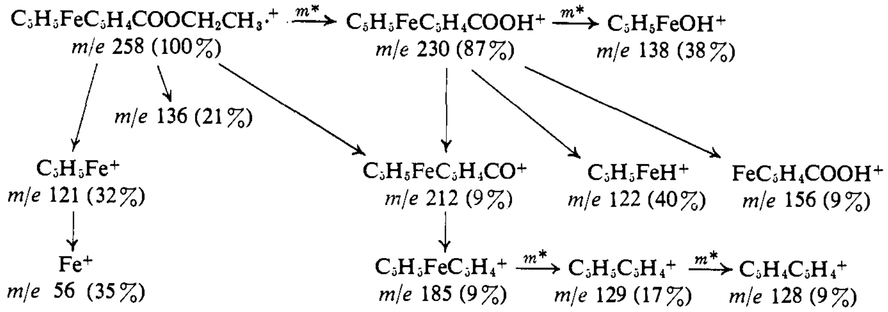
Finally, the spectra of ethyl δ-ferrocenylvalerate and ethyl ϵ-ferrocenylcaproate (Schemes X and XI) are analogous to those of the methyl esters, with the exception of the loss of ethylene from the molecular ion.

The Isotope Effect. We previously observed the absence of an isotope effect in the analogous loss of

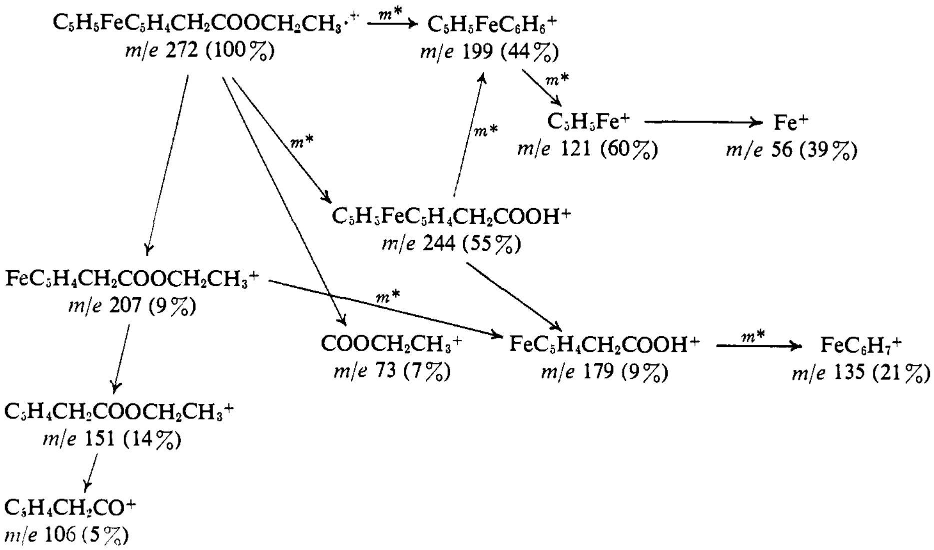
---

[8] Apparently C_3H_3 may also serve as a ligand in ions produced subsequent to ion–molecule reactions of ferrocene and nickelocene: E. Schumacher and R. Taubenest, *Helv. Chim. Acta*, 47, 1525 (1964).

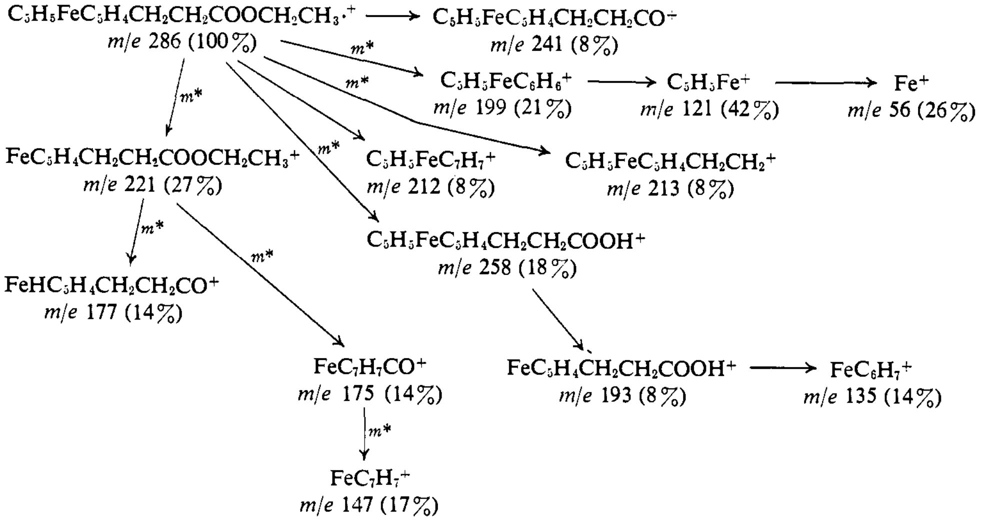
Scheme VI



Scheme VII



Scheme VIII



CH_2O from $(M - C_5H_5)^+$ in methyl *o*-ferrocenylbenzoate but the presence of an effect in the *o*-ferrocenylphenylacetate ester.[2] The data below are for the esters where $n = 2$ and $n = 3$ which, on the basis of the number of carbons intervening between the ester function and the ferrocene moiety, should be similar to those for the benzoate and phenylacetate, respectively. They are reported in terms of the peak intensity ratio[9] 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[10] (Table II).

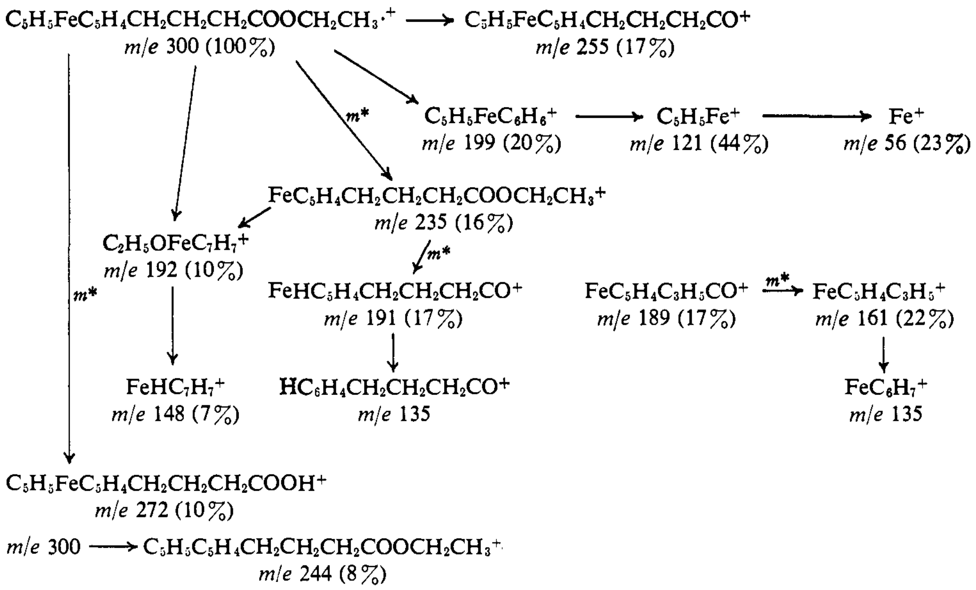
Once again the similarity of the ferrocenylpropionate to the ferrocenylbenzoate and of the ferrocenylbutyrate to the ferrocenylphenylacetate, in terms of details of the mechanism, is brought forth. The absence of an isotope effect is noted in both cases where there are two intervening carbons and suggests prior formation of a complex between the ferrocene unit and the hydrogen to be transferred before the rate-determining step of the rearrangement, as was suggested for the diaryl-

---

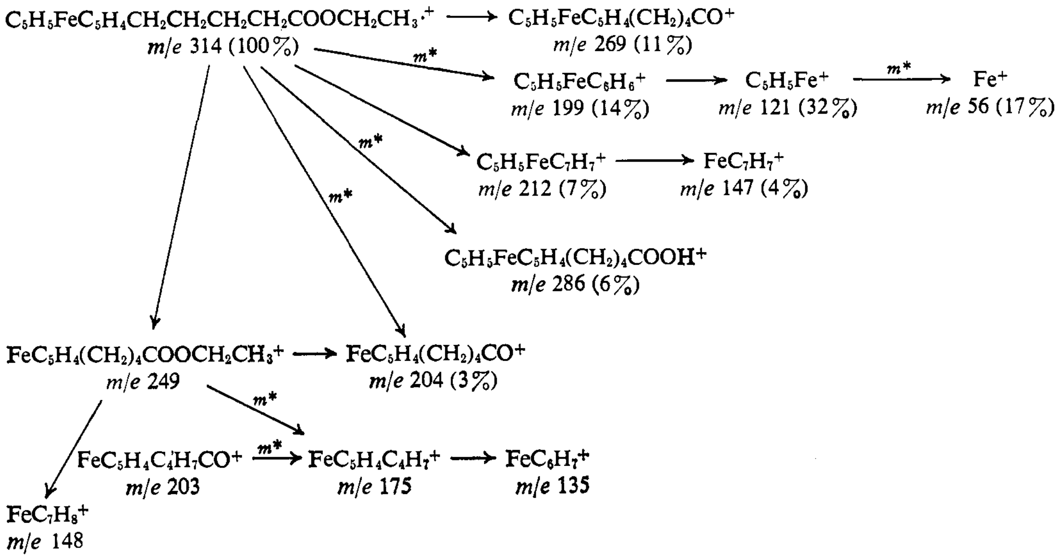
(9) M. M. Bursey and F. W. McLafferty, *J. Am. Chem. Soc.*, **88**, 529 (1966).

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

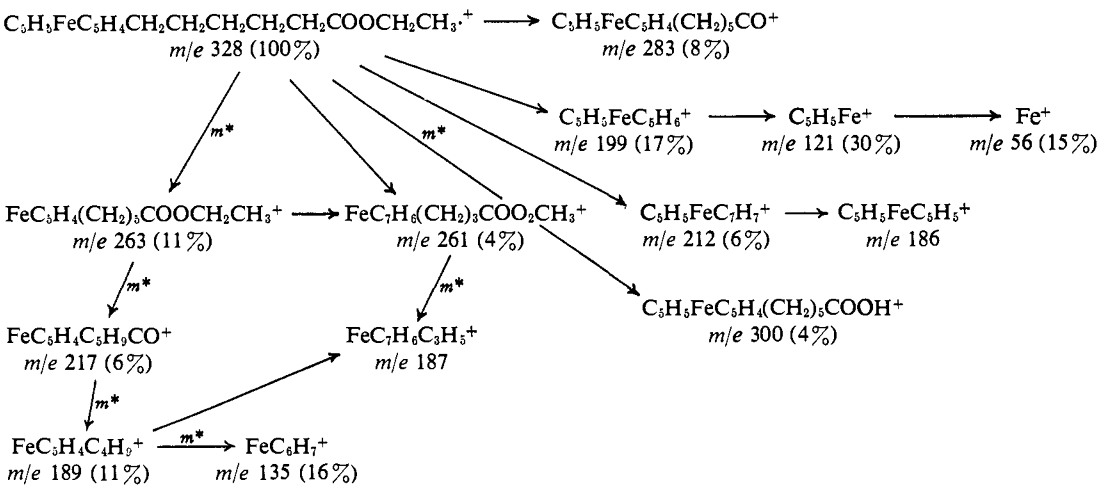
Scheme IX



Scheme X



Scheme XI

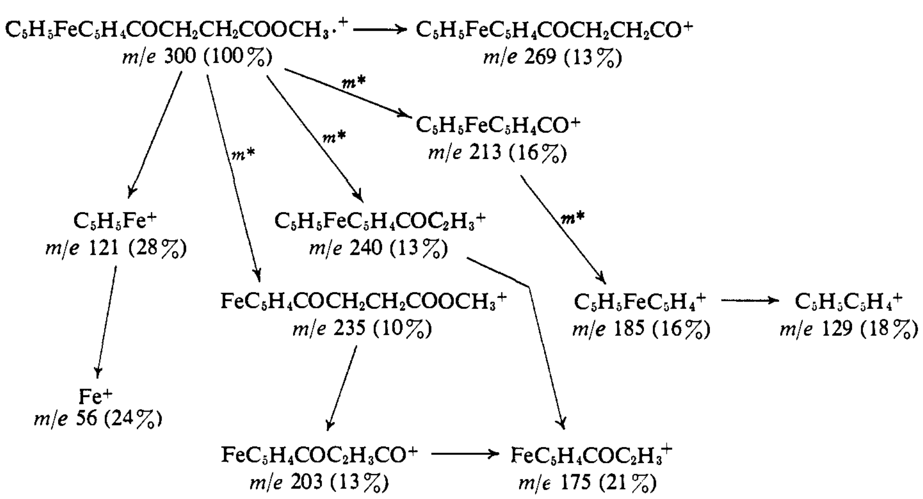


methane system.[11] In the cases where three carbons intervene, both compounds show an isotope effect of similar proportions, relatively constant over the voltage range studied in both cases. The data may again be incorporated into a scheme where C–D bond rupture occurs in the rate-determining step, although it is un-

---

(11) S. Meyerson, H. Drews, and E. K. Fields, *J. Am. Chem. Soc.*, **86**, 4964 (1964).

Scheme XII



certain whether the complex forms prior to this rupture or whether C–O bond rupture is concerted with C–D rupture.

In the case of methyl ferrocenecarboxylate, the first result from labeling studies indicated scrambling of the hydrogens prior to loss of CH_2O from $CH_3OFeC_5H_5^+$. A low-voltage study of the extent of scrambling is presented in Table III, where the data are once again given in terms of intensity ratios. It is evident that the simple mechanism, in which loss of formaldehyde occurs before scrambling can take place, that is, in which CD_2O is lost instead of CH_2O or CHDO, is even less favored at lower voltages than at 75 v. There are at least two mechanisms operating: one which is approximated by the absence of scrambling and another approximated fairly well by the scrambling of four ring hydrogens and three methoxy hydrogens. The latter approximation is suggested by the relative constancy of the ratios of loss of the three species at the last three voltages examined.

Table II. Low-Voltage Intensity Ratio in the Mass Spectra of Propionate and Butyrate Esters

Fractional intensity of CO_2	[177]/[207], $FcCH_2CH_2COOCH_3$	[178]/[210], $FcCH_2CH_2COOCD_3$
1.00	0.27	0.27
0.20	0.14	0.15
0.085	0.12	0.12
0.04	0.086	0.085
0.01	0.036	0.035
	[191]/[221], $FcCH_2CH_2CH_2COOCH_3$	[192]/[224], $FcCH_2CH_2CH_2COOCD_3$
1.00	0.44	0.35
0.20	0.20	0.16
0.10	0.14	0.11
0.05	0.11	0.085
0.01	0.07	0.05

Table III. Low-Voltage Intensity Ratios in the Mass Spectrum of $FcCOOCD_3$[a]

Fractional intensity of CO_2	$\frac{[A - CH_2O]}{[A]}$	$\frac{[A - CHDO]}{[A]}$	$\frac{[A - CD_2O]}{[A]}$
1.00	0.36	0.55	0.54
0.30	0.22	0.30	0.22
0.14	0.17	0.22	0.10
0.075	0.15	0.17	0.07
0.043	0.12	0.135	0.055
0.007	0.048	0.052	0.020

[a] Where A = $CD_3OFeC_5H_5$.

The final example, where it was noted that CH_2O was apparently lost without scrambling from $CH_3OFeC_5H_5^+$, is that of methyl ferrocenylacetate. The data in Table IV indicate that a small isotope effect appears even down to low voltages and that prior formation of a complex need not be invoked to rationalize the data. The large differences between the data found for the decompositions of the ions written as $CH_3OFeC_5H_5^+$ certainly indicate that these have quite different properties, and possibly different structures, depending on whether they are formed from the ferrocenecarboxylate ester or the ferrocenylacetate ester.

Table IV. Low-Voltage Intensity Ratios in the Mass Spectra of $FcCH_2COOCH_3$ and $FcCH_2COOCD_3$

Fractional intensity of CO_2	[135]/[165], $FcCH_2COOCH_3$	[136]/[168], $FcCH_2COOCD_3$
1.00	2.6	2.4
0.20	0.95	1.0
0.10	0.64	0.58
0.05	0.57	0.48

Correspondence with Solution Phenomena. Studies of cyclization of ω-ferrocenylalkanoic acids[12] suggest that when $n = 2$, 3, or 4 in $Fc(CH_2)_nCOOH$, cyclic ketones may be formed. For $n = 2$, the heteroannularly cyclized product is obtained; for $n = 3$ or 4, the homoannularly cyclized product is obtained. The cases where $n = 2$ or 3 correspond to a six-membered transition state, the latter to a seven-membered transition state. We have remarked earlier[2] that the reactions where CH_2O is lost from $(M - C_5H_5)^+$ do not fit neatly into a picture of a transition state including a six-membered ring. The only case in which a six-membered ring may easily be drawn, where $n = 0$, is greatly complicated by the ready exchange of protons and deuterons before formaldehyde is lost.

---

(12) K. L. Rinehart, Jr., R. J. Curby, Jr., D. H. Gustafson, K. G. Harrison, R. E. Bozak, and D. E. Bublitz, *J. Am. Chem. Soc.*, **84**, 3263 (1962).

In the cases where CH_3O is apparently transferred, no exchange occurs when $n = 1$ or 2. These cases correspond to a five- and six-membered transition state, respectively; when n is greater or less than these values, transfer seems to occur after partial randomization of hydrogen. In these cases the specificity seems to parallel expectations from solution behavior to some extent.

The closest analogy appears to be with the mass spectral results noted earlier.[2] It is not to be expected, of course, that nmr shifts would be of value in establishing this similarity, since the flexibility of the carbon chain allows the methyl group to spend most of the time away from the shielding cone associated[13,14] with the ferrocene nucleus. Consequently, the nmr shifts do not sufficiently reflect the ability of these methyl groups to approach the ferrocene nucleus for bonding. Nevertheless, if the protons spend even a small amount of time near the metallocene nucleus, they must be considered candidates for transfer. In this light, it is interesting to observe the behavior of methyl β-ferrocenoylpropionate (Scheme XII), in which a carbonyl group separates the alkyl chain from the metallocene nucleus. Models indicate that in the ground state the presence of the carbonyl group permits the molecule only conformations in which the methoxy group is at some distance from the metallocene nucleus. As a result, transfer reactions might not be expected if the geometry of the ions preceding the rearrangements were similar to the same features of the molecule in solution; in fact, they are not observed.

Experimental Section

General. Melting points above room temperature were determined on a Kofler hot stage and those below room temperature in an oil bath cooled to 0° and warmed by standing and are uncorrected. Infrared spectra were recorded from samples in KBr pellets or on salt plates 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 voltages were recorded with a 2-μa target current and a 0.5-v repeller voltage. The oven was maintained at 185° and the source at 175°. The analyses were performed by Alfred Bernhardt, 433 Mülheim (Ruhr), Germany.

Methyl Ferrocenylcarboxylate. The following procedure for the formation of the various esters was used in all similar preparations and therefore will be presented for this preparation alone.

To a solution of 230 mg (1.0 mmole) of ferrocenecarboxylic acid, mp 210° dec (lit.[15] mp 210° dec), and 3.0 ml of methanol was added 0.5 ml of $BF_3 \cdot Et_2O$.[16] The solution was refluxed for 2 hr, cooled, and poured into 10 ml of saturated $NaHCO_3$ solution. The organic layer was washed with water and dried over $MgSO_4$ and the ether was stripped, yielding 195 mg (80%). Filtering through alumina and recrystallization from hexane yielded a product of mp 68.5–70° (lit.[17] mp 70–71°).

Trideuteriomethyl ferrocenylcarboxylate was prepared from 100 mg of ferrocenylcarboxylic acid (0.44 mmole) and 1.5 ml of trideuteriomethyl alcohol (Merck Sharp and Dohme of Canada), yielding 90 mg (85%) upon recrystallization from hexane, mp 68–70°.

Methyl ferrocenylacetate was prepared from 244 mg (1.0 mmole) of ferrocenylacetic acid, mp 149–53° (lit.[18,19] mp 152–156° dec), by stirring at room temperature 1 hr, yielding 185 mg (72%) upon recrystallization from hexane; mp 20–21°; ν^{film} 3085, 1735, 1105, and 1001 cm^{-1}; nmr, τ 6.69 (s, CH_2), 6.32 (s, CH_3), 5.90 (s, C_5H_5), and 5.87 (s, C_5H_4); mol wt (mass spectrometry), 258. This compound rapidly decomposed above its melting point.

Trideuteriomethyl ferrocenylacetate was prepared from 100 mg (0.41 mmole) of ferrocenylacetic acid and 1.5 ml of trideuteriomethyl alcohol, yielding 91 mg (84%) upon recrystallization from hexane, mp 20–21°.

Methyl ferrocenylpropionate was prepared from 258 mg (1.0 mmole) of ferrocenylpropionic acid, mp 115–117° (lit.[18] mp 115–116), yielding 252 mg (93%) upon recrystallization from hexane, mp 36–37° (lit.[20] mp 36–38°).

Trideuteriomethyl β-ferrocenylpropionate was prepared from 100 mg of ferrocenylpropionic acid (0.39 mmole) and 1.5 ml of trideuteriomethyl alcohol, yielding 103 mg (97%) upon recrystallization from hexane, mp 36–37°.

Methyl γ-ferrocenylbutyrate was prepared from 272 mg (1.0 mmole) of γ-ferrocenylbutyric acid, mp 117–118° (lit.[18] mp 115–116°), yielding 270 mg (94%) upon recrystallization from hexane, mp 20°; lit.[21] bp 168–170° (4 mm).

Trideuteriomethyl γ-ferrocenylbutyrate was prepared from 100 mg of γ-ferrocenylbutyric acid (0.37 mmole) and 1.5 ml of trideuteriomethyl alcohol, yielding 102 mg (95%) upon recrystallization from hexane, mp 20–21°.

Methyl δ-ferrocenylvalerate was prepared from 286 mg (1.0 mmole) of δ-ferrocenylvaleric acid, mp 106–108° (lit.[18] mp 109–110°), yielding 267 mg (88%) upon recrystallization from hexane: mp 32–33°; ν^{KBr} 3085, 1735, 1105, and 1003 cm^{-1}; nmr, τ 8.41 (m, CH_2CH_2), 7.70 (m, CH_2, CH_2), 6.32 (s, CH_3), 5.94 (broad s, C_5H_4), and 5.90 (s, C_5H_5).

Anal. Calcd for $C_{16}H_{20}O_2Fe$: C, 64.02; 6.72. Found: C, 63.85; H, 6.87.

Methyl ϵ-ferrocenylcaproate was prepared from 300 mg (1.0 mmole) of ϵ-ferrocenylcaproic acid, mp 86–90° (lit.[18] mp 83–84, 92–93°), yielding 274 mg (88%) upon recrystallization from hexane: mp 20–23°; ν^{film} 3085, 1735, 1107, and 1004 cm^{-1}; nmr, τ 8.52 (m, $CH_2CH_2CH_2$), 7.72 (m, CH_2, CH_2), 6.38 (s, CH_3), 5.97 (broad s, C_5H_4), and 5.93 (s, C_5H_5).

Anal. Calcd for $C_{17}H_{22}O_2Fe$: C, 64.98; H, 7.06. Found: C, 64.98; H, 6.96.

Ethyl ferrocenylcarboxylate was prepared from 230 mg of ferrocenecarboxylic acid (1.0 mmole), yielding 234 mg (91%) upon recrystallization from hexane, mp 60–61.5° (lit.[22] mp 61–62°).

Ethyl ferrocenylacetate was prepared from 244 mg of ferrocenylacetic acid (1.0 mmole), yielding 185 mg (68%) upon recrystallization from hexane: mp 29–29.5°; ν^{film} 3085, 1735, 1110, and 1005 cm^{-1}; nmr, τ 8.75 (t, CH_3), 6.70 (s, CH_2), 5.90 (s, C_5H_5), 5.89 (m, C_5H_4), 5.84 (q, CH_2); mol wt (mass spectrometry), 272. This compound rapidly decomposed above its melting point.

Ethyl β-ferrocenylpropionate was prepared from 258 mg of ferrocenylpropionic acid (1.0 mmole), yielding 262 mg (92%) upon recrystallization from hexane, mp 24.5–25.5° (lit.[23] mp 25–26°).

Ethyl γ-ferrocenylbutyrate was prepared from 272 mg of γ-ferrocenylbutyric acid (1.0 mmole), yielding 268 mg (89%) upon recrystallization from hexane: mp 15–17 (lit.[21] mp 40–42°); ν^{film} 3085, 1730, 1110, and 1005 cm^{-1}; nmr, τ 8.72 (t, CH_3), 8.22 (m, CH_2), 7.70 (m, CH_2, CH_2), 5.95 (broad s, C_5H_4), 5.90 (s, C_5H_5), and 5.85 (q, CH_2). Several ferrocene esters have more than one melting point and this must be one.

Ethyl δ-ferrocenylvalerate was prepared from 286 mg of δ-ferrocenylvaleric acid (1.0 mmole), yielding 273 mg (87%) upon recrystallization from hexane: mp 15–17°; ν^{film} 3085, 1730, 1107, and 1003 cm^{-1}; nmr, τ 8.74 (t, CH_3), 8.40 (m, CH_2CH_2), 7.70 (m, CH_2, CH_2), 5.92 (broad s, C_5H_4), 5.89 (s, C_5H_5), and 5.82 (q, CH_2).

Anal. Calcd for $C_{17}H_{22}O_2Fe$: C, 64.98; H, 7.06. Found: C, 64.82; H, 7.21.

---

(13) L. N. Mulay and M. E. Fox, *J. Am. Chem. Soc.*, **84**, 1308 (1962).

(14) L. N. Mulay and M. E. Fox, *J. Chem. Phys.*, **38**, 760 (1963).

(15) W. F. Little and R. Eisenthal, *J. Am. Chem. Soc.*, **82**, 1577 (1960).

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

(17) R. A. Benkeser, D. Goggin, and G. Schroll, *J. Am. Chem. Soc.*, **76**, 4025 (1954).

(18) K. L. Rinehart, Jr., R. J. Curby, Jr., and P. E. Sokol, *ibid.*, **79**, 3420 (1957).

(19) D. Lednicer, J. K. Lindsey, and C. Hauser, *J. Org. Chem.*, **23**, 653 (1958).

(20) K. Schlögl, M. Peterlik, and H. Seiler, *Monatsh.*, **93**, 1309 (1962).

(21) J. B. Thomson, *Chem. Ind.* (London), 1122 (1959).

(22) V. Weinmayr, *J. Am. Chem. Soc.*, 77, 3009 (1955).

(23) K. Schlögl and H. Seiler, *Monatsh.*, 91, 79 (1960).

Ethyl ε-ferrocenylcaproate was prepared from 300 mg (1.0 mmole) of ε-ferrocenylcaproic acid, yielding 285 mg (88%), and was recrystallized from hexane: mp 27.5–29°; ν^{KBr} 3085, 1735, 1110, and 1008 cm^{-1}; nmr, τ 8.77 (t, CH_3), 8.54 (m, $CH_2CH_2CH_2$), 7.72 (m, CH_2, CH_2), 5.98 (broad s, C_5H_4), 5.93 (s, C_5H_5), and 5.89 (q, CH_2).

Anal. Calcd for $C_{18}H_{24}O_2Fe$: C, 65.86; H, 7.37. Found: C, 66.35; H, 7.43.

Methyl β-ferrocenoylpropionate was prepared from 286 mg (1.0 mmole) of β-ferrocenoylpropionic acid, mp 166–169° (lit.[18] mp 166.5–167.5°), yielding 224 mg (75%) upon recrystallization from hexane, mp 60–61° (lit.[23] mp 60°).

Acknowledgments. We thank Messrs. Laurence R. Dusold and Thomas A. Elwood for recording many of the spectra. D. T. R. thanks E. I. du Pont de Nemours and Co., Inc., for a Du Pont Teaching Fellowship and the American Enka Corp. for an Enka Summer Fellowship.

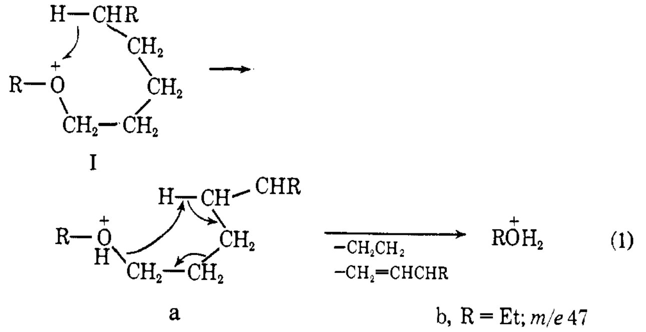
Mass Spectrometry in Structural and Stereochemical Problems. CXLIII.[1] Unusual Fragmentations in the Mass Spectra of Some Aliphatic Ethers[2]

Wayne Carpenter,[3] A. M. Duffield, and Carl Djerassi

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305. *Received June 26, 1967*

Abstract: The mass spectra of a series of aliphatic ethers ROR′ (R′ ⩾ n-C_5) contain a peak involving transfer of two hydrogen atoms from R′ such that the charged species formally corresponds to ROH_2. In ethyl n-hexyl ether deuterium labeling demonstrated that the major amounts of both transferred hydrogen atoms arise from C-5 of the hexyl chain and that a seven-membered intermediate is preferred over all other ring sizes. A mechanistic rationalization is presented for this fragmentation and for the loss of ethanol from ethyl n-hexyl ether which proceeds preferentially through five- and six-membered intermediates.

The first detailed study of the electron impact promoted decomposition of aliphatic ethers is due to McLafferty.[4] Further work,[5] utilizing deuterium labeling, delineated some of the hydrogen rearrangement processes occurring during the mass spectrometric fragmentation of aliphatic ethers. During this study,[5,6] an interesting peak in the mass spectrum of ethyl n-hexyl ether was observed at m/e 47 which formally corresponds[6] to protonated ethyl alcohol and must involve a double hydrogen migration from the hexyl chain. At the time of our previous publication,[5] the origin of this peak was not commented upon since the requisite deuterium labeling of the hexyl chain remained to be completed. We have now determined that this apparently bizarre rearrangement is in fact of general occurrence in aliphatic ethers provided one alkyl chain possesses at least five carbon atoms and, furthermore, that this rearrangement is enhanced at low ionizing voltages. Spiteller-Friedmann and Spiteller[7] observed the same phenomena in symmetrical dialkyl ethers and suggested the mechanism given in (1) without the benefits of deuterium labeling.



The present study utilizing deuterium labeling of all positions of the hexyl chain of ethyl n-hexyl ether (IV) invalidates the above proposal for all but a minor portion (17%, see Table I) of the ion yield at m/e 47.

The mass spectra of seven aliphatic ethers with at least one n-alkyl chain of five carbon atoms or longer have been measured and all display evidence of a peak corresponding to $(ROH_2)^+$ (Table II). At low electron energy these peaks all increase in ion yield relative to the values obtained with 70-ev electrons.

Mass Spectra of Deuterated Analogs of Ethyl n-Hexyl Ether. The mass spectra of ethyl n-hexyl ether taken at 70 and 12 ev using a heated inlet system (ion source temperature 200°) are reproduced in Figures 1 and 2. It will be observed that at high electron voltage (Figure 1) the molecular ion peak (m/e 130) is of low abundance and that a substantial M − 1 fragment is obtained. If, however, the spectrum (Figure 3) is repeated using direct sample insertion into a relatively cold (70°) ion source, a much more pronounced molecular ion is obtained and virtually no M − 1 fragment is visible. The Spitellers have already commented in

---

[1] Part CXLII: W. S. Briggs and C. Djerassi, *J. Org. Chem.*, in press.

[2] Financial assistance (Grant No. AM-04257) from the National Institutes of Health of the U. S. Public Health Service is gratefully acknowledged. The purchase of the Atlas CH-4 mass spectrometer was made possible by National Aeronautics and Space Administration Grant NsG 81-60.

[3] Recipient of a Senior Postdoctoral Fellowship while on leave from the U. S. Naval Ordnance Test Station, China Lake, Calif.

[4] F. W. McLafferty, *Anal. Chem.*, **29**, 1782 (1957).

[5] C. Djerassi and C. Fenselau, *J. Am. Chem. Soc.*, **87**, 5747 (1965).

[6] C. Fenselau, Ph.D. Thesis, Stanford University, 1965, pp 37, 46, 47, and 61.

[7] M. Spiteller-Friedmann and G. Spiteller, *Chem. Ber.*, **100**, 79 (1967).