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The Mass Spectra of Several Ferrocenoyl Compounds

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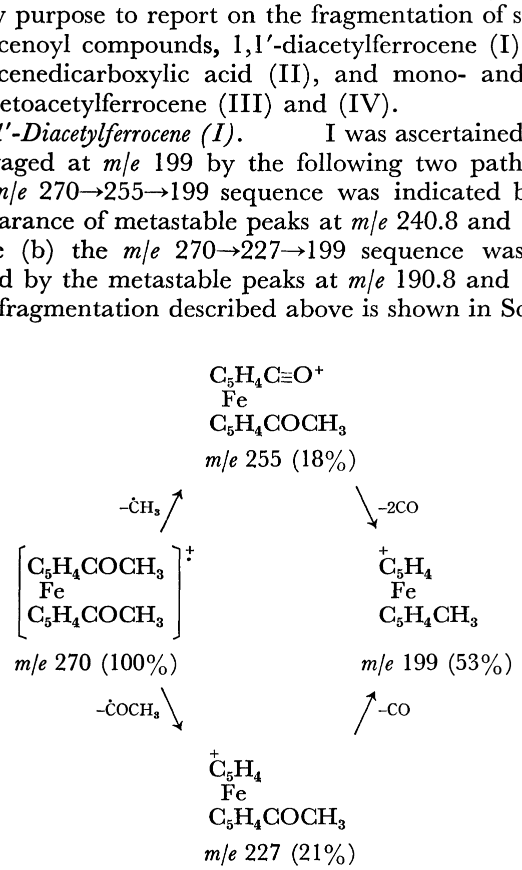
Since 1955, beginning with the work of Friedman *et al.*,[1] some reports on the mass spectra of ferrocene[2-4] and its derivatives[5,6] have appeared. The fragmentation of disubstituted ferrocenoyl compounds has never been reported, however, though the mass spectra of some monosubstituted ferrocenoyl compounds has examined by Mandelbaum and Cais.[6] In this paper, it is my purpose to report on the fragmentation of several ferrocenoyl compounds, 1,1′-diacetylferrocene (I), 1,1′-ferrocenedicarboxylic acid (II), and mono- and 1,1′-bisacetoacetylferrocene (III) and (IV).

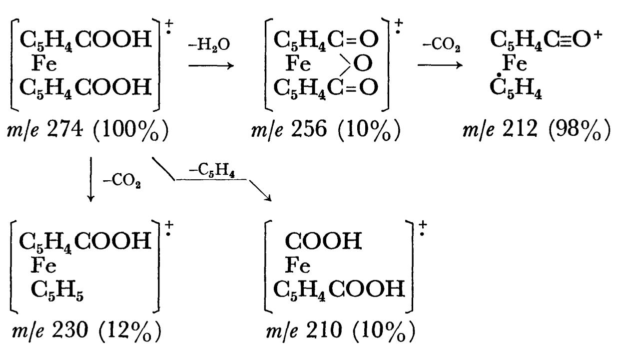
1,1′-Diacetylferrocene (I). I was ascertained to be cleavaged at m/e 199 by the following two paths: (a) the m/e 270→255→199 sequence was indicated by the appearance of metastable peaks at m/e 240.8 and 155.3, while (b) the m/e 270→227→199 sequence was suggested by the metastable peaks at m/e 190.8 and 174.4. The fragmentation described above is shown in Scheme 1.



Scheme 1

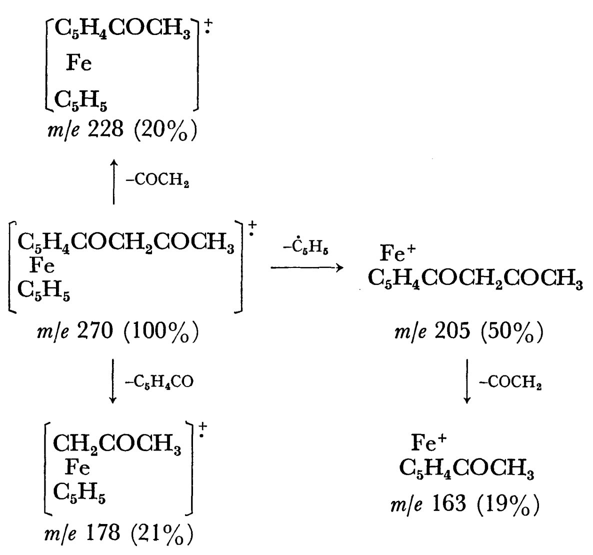
The m/e 163 ($Fe^+C_5H_4COCH_3$), which appeared in the spectrum of monoacetylferrocene,[6] was also observed (relative intensity 19%) in the spectrum of I. This fragment ion might be produced by the loss of $\dot{C}_5H_4COCH_3$ from the molecular ion or by that of C_5H_4 from the m/e 227.

1,1′-Ferrocenedicarboxylic Acid (II). The following fragmentation was observed from the spectrum of II: (a) a sequence of m/e 274→256 (molecular ion of anhydride of II)→212, supported by the metastable peaks at m/e 239.2 and 175.6, corresponding to the loss of water and carbon dioxide in that order, and (b) the m/e 230 corresponding to the molecular ion of ferrocenemonocarboxylic acid and the rearrangement ion, m/e 210, produced from the m/e 274 by the loss of carbon dioxide and C_5H_4 respectively. This m/e 230 might be transferred to the fragment ion of $Fe^+C_5H_4COOH$ (m/e 165, 39%) and $HOFeC_5H_5$ (m/e 138, 25%), as has been reported by Mandelbaum and Cais.[6] The main paths of the fragmentation are shown in Scheme 2.



Scheme 2

Mono- and 1,1′-Bisacetoacetylferrocene (III) and (IV). There are three routes for the cleavage of III: (a) the m/e 270→205→163 sequence was supported by the metastable peaks at m/e 155.6 and 129.6, (b) the m/e 228 appeared upon the loss of $COCH_2$ from the m/e 270 (a metastable peak at m/e 192.5), (c) the rearrangement ion, m/e 178, appeared upon the loss of C_5H_4CO from



Scheme 3

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1) L. Friedman, A. P. Irsa, and G. Wilkinson, *J. Amer. Chem. Soc.*, **77**, 3689 (1955).

2) E. Schumacher and R. Taubenest, *Helv. Chim. Acta*, **47**, 1525 (1964).

3) R. G. Denning and R. A. D. Wentworth, *J. Amer. Chem. Soc.*, **88**, 4619 (1966).

4) J. Mueller and L. D'or, *J. Organometal. Chem.*, **10**, 313 (1967).

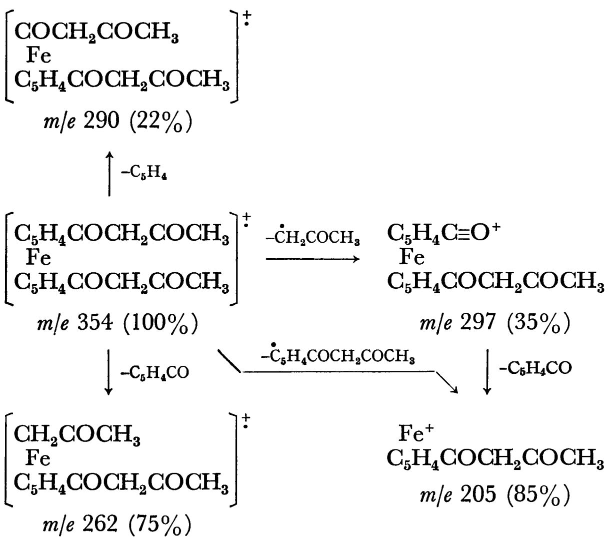
5) D. T. Roberts, W. F. Little, and M. M. Bursey, *J. Amer. Chem. Soc.*, **89**, 4917, 6156 (1967).

6) A. Mandelbaum and M. Cais, *Tetrahedron Lett.*, **51**, 3847 (1964).

the m/e 270 (a metastable peak at m/e 117.3). These results are given in Scheme 3.

It can be presumed that the m/e 228 corresponding to molecular ion of monoacetylferrocene is decomposed to $C_5H_5FeC_5H_4C{\equiv}O^+$ (m/e 213, 12%) or $Fe^+C_5H_4COCH_3$ (m/e 163, 19%) upon the loss of $\dot{C}H_3$ or $\dot{C}_5H_5$,[6] while the m/e 178 resulting from the rearrangement is decomposed to $Fe^+CH_2COCH_3$ (m/e 113, 5.2%).

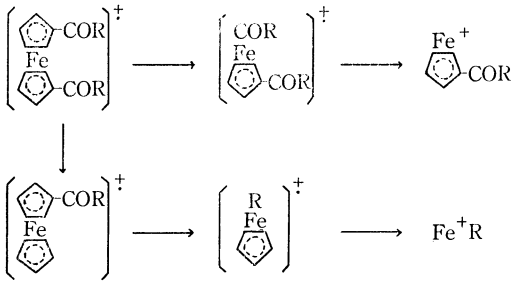
The fragmentation of IV can be explained as follows: (a) the m/e 354→297→205 sequence was supported by the metastable peaks at m/e 249.2 and 141.5, while the m/e 205 was formed by the loss of $\dot{C}_5H_4COCH_2COCH_3$ from the m/e 354 (a metastable peak at m/e 118.7), and (b) both rearrangement ions, m/e 290 and 262, were formed from the m/e 354 by the loss of C_5H_4 and C_5H_4CO respectively (a metastable ion at m/e 235.9 for 354→290 and m/e 193.9 for 354→262). These results are shown in Scheme 4.



Scheme 4

Both ions of m/e 290 and 262 might be also transferred to m/e 205. This m/e 205 would seem to be further decomposed by a path similar to that shown in Scheme 3 because of the appearance of the m/e 163 (46%). As the other fragment ions, the m/e 270 (12%), corresponding to the molecular ion of I or III, and the m/e 178 (20%), which was confirmed by the cleavage of III, were observed in the spectrum.

The above results can be summarized as follows. (1) For the mono- and 1,1′-di-substituted ferrocenoyl compounds, II, III, and IV, but not I, the common mechanisms by which the rearrangement ions appear are given by:



(R=OH or CH_2COCH_3)

(2) The fragment ions, such as $C_5H_5Fe^+C_5H_4$ (m/e 185), $\dot{C}_5H_4Fe^+C_5H_4$ (m/e 184), $Fe^+C_5H_5$ (m/e 121), $Fe^+\dot{C}_5H_4$ (m/e 120), and Fe^+ (m/e 56), observed by Mandelbaum *et al.*[6] were also observed by the cleavages of the fragment ions shown in Schemes 1, 2, 3, and 4.

Experimental

The mass spectra were obtained by means of a Japan Electron Optics Co., Ltd., JMS-01SG Mattauch-Herzog double-focussing mass spectrometer, at an ionizing voltage of 75 V, an emission current of 100 μA, and an accelerating voltage of 6.4 kV. The oven was maintained at 150°C.

1,1′-Diacetylferrocene (I). I was prepared from ferrocene by the method of Rosenblum and Woodward.[7] Recrystallization from benzene yielded a product with a mp of 130—131°C (lit,[7] mp 130—131°C).

1,1′-Ferrocenedicarboxylic Acid (II). II was prepared from I using the iodine-oxidation method.[8] The refined product decomposed at about 250°C (lit,[8] at more than 240°C decomp.).

Monoacetoacetylferrocene (III). III was prepared by the condensation of ethyl acetate with monoacetylferrocene in the presence of sodium amide.[9] Recrystallization from *n*-hexane yielded a product with a mp of 97—98°C (lit,[10] mp 97.5—98.5°C).

1,1′-Bisacetoacetylferrocene (IV). IV was prepared from I by the same method as III. Recrystallization from benzene yielded a product with a mp of 143—144°C (lit,[11] mp 142.5—144°C).

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