Charge Distribution Between Formally Identical Fragments: The McLafferty Rearrangement

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The McLafferty rearrangement for 2,5-diphenyl-1-hexene and its deuterium labelled analogues has been investigated. The α -methylstyrene fragments originating from different parts of the molecular ion retain the charge with equal probability and afford identical metastable spectra. The geometry of the transition state is discussed.

INTRODUCTION

Since its discovery, the McLafferty rearrangement has been the subject of numerous investigations; a recent review article on the topic is available.¹ The transition state of the McLafferty reaction has been studied from a theoretical point of view by Dougherty² and by Boer et al.³ Dougherty employed the perturbation molecular orbital (PMO) approach for the molecular ion of 1-pentene and proposed a concerted mechanism. On the other hand, Boer et al., who made use of Mulliken's MO method, concluded that the optimal reaction path for the McLafferty rearrangement of the molecular ion of pentanal is stepwise: first the γ hydrogen is transferred to the carbonyl oxygen and then the β -bond is cleaved. The two mechanisms differ in the geometrical arrangement of bonds: Dougherty's mechanism requires the double bond to be twisted in order to achieve the best overlap of the forming C-H and the splitting C-C bonds, while in Boer's mechanism, the transition state is essentially planar. The stepwise mechanism is generally accepted at present¹ and it has received some experimental support.4

A simple experiment can be conducted to check Dougherty's conclusions concerning terminal olefins. In the case of an ion $[AB]^+$, which decomposes via the McLafferty reaction to two formally identical fragments A and B (Scheme 1), there are two reaction paths:

$$[AB]^{+} \rightarrow [A]^{+} + B$$
 and/or $[AB]^{+} \rightarrow A + [B]^{+}$

If A and B are virtually identical, each should carry the charge with an equal probability according to Stevenson's rule.⁵ This is the case with Boer's mechanism by which both $[A]^{++}$ and $[B]^{++}$ can be formed with the same structure and in the same electronic state. On the contrary, Dougherty's mechanism requires the double bond in A to be twisted. Thus, A is produced in an excited state, while B is in the ground state. Hence, A would have a lower ionization energy and would be charged preferentially to conform to Steven-



son's rule. A variety of model alkenes AB could be devised, A and B being distinguished by D or ¹³C labelling. The mass spectrum of $(6,6,6-D_3)$ -2-methyl-5-([D₃]-methyl)-1-hexene has been reported in a paper by Mayer and Djerassi.⁶ In this spectrum the abundance of the [C₄H₈]⁺⁺ ions (part A) is about 20% higher than that of C₄H₂D₆ (part B). As the [C₄H₈]⁺⁺ ion could have precursors other than the molecular ion, no definite conclusion could be reached from the published spectrum.

RESULTS AND DISCUSSION

In the present paper we have used 2,5-diphenyl-1hexene 1 and its labelled derivatives 2, 3, and 4



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(Table 1). Figure 1 shows that **1** fragments cleanly via the McLafferty reaction; the $[C_9H_{10}]^+$ ion represents 46.4, 57.9, 72.5 and 80.6% of the total ion current at 75, 25, 20 and 16 eV, respectively. The γ -benzylic hydrogen is transferred to part A of the molecular ion, the specificity being higher than 95%, as deduced from the spectrum of 4. The regiospecificity remains unchanged in the range 14-75 eV. Both the subunits A and B must be labelled in this case to make them discernible. The charge distribution between A and Bcan be expressed conveniently as the abundance ratio $k = [B]^{+}/[A]^{+}$. Table 2 shows that k = 1 within experimental error for 2, 3, and 4, regardless of both the ionizing energy and the positions of deuterium atoms. This is compatible either with Boer's mechanism or with any other mechanism which produces A and Bwith the same ionization energy. Provided that Dougherty's geometry of the transition state is the best for the concerted mechanism, the latter could be dismissed.

Both the origins and further decompositions of $[A]^{+\cdot}$ and $[B]^{+\cdot}$ have been investigated in some detail. The ratio k reflects the charge distribution between A and B adequately only if both intensities $[A]^{+\cdot}$ and $[B]^{+\cdot}$ are governed mainly by the rate of their formation from the single parent ion $[AB]^{+\cdot}$. Indeed, in the metastable spectra of both $[A]^{+\cdot}$ and $[B]^{+\cdot}$ [decompositions in the 1st field free region (FFR)], there is only one signal corresponding to the decomposition of the molecular ion. Both $[A]^{+\cdot}$ and $[B]^{+\cdot}$ decompose further

Table 1. Deuterium contents in 2, 3 and 4

Compound	D ₅	D4	D ₃	D ₂	D ₁	Do
2		9.4	27.5	59.2	3.9	—
3	86.4	10.8	2.8			
4	5.3	42.0	46.3	6.4		—

Table 2. Abundance ratios $k = [B]^{+}/[A]^{+*a}$

				EI	ectron	k energ	ıv (eV)	
Compound	75	25	20	18	17	16	15	14
2	1.01	1.00	0.99	0.99	0.98	0.98	0.99	1.03
3 4	1.00	1.00	0.97 1.01	0.98	0.99	1.01	1.05	1.00

^a The intensities have been corrected for ¹³C contributions.

by loss of H, CH₃, C₂H₃ and C₃H₅. When accounting for the mass shifts due to the labelling, $[A]^{+\cdot}$ and $[B]^{+\cdot}$ gave almost identical metastable spectra in the 2nd FFR. The abundance ratio k is not affected by correcting the intensities of $[A]^{+\cdot}$ and $[B]^{+\cdot}$ for the loss of hydrogen. It means that $[A]^{+\cdot}$ and $[B]^{+\cdot}$ lose hydrogen and/or deuterium to the same extent so that isotope effects can be neglected. Table 3 shows that the calculated deuterium contents of the ions $[A]^{+\cdot}$ are close to those of the corresponding molecular ions.

Although the charge distribution seems to be expressed reasonably by the abundance ratio $[B]^+/[A]^+$, there are other effects which must be considered. The γ -hydrogen transfer can be followed by subsequent

Table 3. Deuterium contents of fons [A]	Table	. Deuterium conte	ents of ions	[A] ⁺⁻
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		Electron energy (eV)									
Compou	nd	75	25	20	18	17	16	15	14		
2	D_4	6.0	5.5	5.9	5.5	6.6	5.5	5.7	5.8		
	D_3	26.0	26.1	26.2	27.1	27.2	27.1	28.6	26.8		
	D_2	62.8	62.2	63.2	62.8	61.2	62.7	61.5	62.3		
	D_1	5.2	6.1	4.6	5.1	5.1	4.6	4.2	5.0		
3	D ₅	89.6	89.1	88.7	89.3	89.8	89.6	88.7	8 8 .6		
	D_4	4.8	6.1	8.0	7.9	8.1	8.5	7.1	5.6		
	D_3	5.7	4.7	3.3	2.8	2.1	1.9	4.2	5.8		
								-			

^a The intensities have been corrected for ¹³C and $[A-H]^+$ contributions. The abundance ratios $[A-H]^+/[A]^+$ were used as the correcting factors in the latter corrections.



Figure 1. The mass spectrum of 1.

hydrogen rearrangements occurring in the B part of the molecular ion.7 The greater stability of the rearranged molecular ion when compared with the original structure could be the driving force for such a rearrangement. Fortunately, any further rearrangement in 1-4 is unlikely, because the structure with the electron deficiency at the benzylic carbon C-5 should be preferred over the others. Second, after the McLafferty rearrangement had proceeded via any mechanism, the primary charge distribution could be affected by the resonance charge transfer. Resonance charge transfer can operate at a long distance (1-2 nm)⁸ and it proceeds best when all energy levels of the reacting particles match perfectly, which holds strictly only for atoms. If A and B were produced in different electronic states (by Dougherty's mechanism), resonance charge transfer probably would be much less effective⁸ so that an unsymmetrical charge distribution could be observed.

CONCLUSION

The symmetrical charge distribution between A and B indicates that these fragments are formed by the McLafferty reaction with identical structures and in

the same electronic states. The structural similarity of $[A]^{+}$ and $[B]^{+}$ is supported by their metastable spectra. These findings contradict the concerted mechanism proposed by Dougherty.²

EXPERIMENTAL

Mass spectra were taken on a JEOL JMS D-100 spectrometer, operating at 14-75 eV, using a direct inlet system. The samples were evaporated at 80-90 °C, and the temperature of the ion source was kept at 140 °C. Decompositions of metastable ions in the 1st FFR were monitored by using the accelerating voltage scan method. Decompositions in the 2nd FFR were measured on a MAT 311 spectrometer, using the electrostatic field scan method. Infrared (IR) spectra were measured on a 75 IR Zeiss (Jena) grating spectrometer. The purity of 1-4 was better than 97%, as checked by thin-layer chromatography (Kieselguhr, Merck, chloroform-hexane, 3:8) and gas chromatography mass spectrometry (SE-30, 3% on Chromosorb W, 2 m/3 mm i.d., column temperature 180 °C, injection 200 °C, separator 180 °C). Compounds 1-4 each contained about 2% of biphenyl.

The chemical syntheses are summarized in Scheme 2.



^a BX₃, THF, H₂O₂, NaOH;⁹ ^b TsCl, pyridine; ^c CH₂(COOC₂H₅)₂, NaH, DMF;¹¹ ^d DMSO, H₂O;¹³ ^e LiH, C₆H₅Li, ether;¹⁴ ^f LiH, C₆D₅Li, ether; ^a (C₆H₅)₃P=CH₂, ether;¹⁵ ^hD₂O, LiOD, THF, C₁₀H₂₁N(CH₃)₃Br.

(2-[D₁])-2-Phenylpropanol (5) was prepared by a standard method⁹ using lithium aluminum deuteride to generate deuteroborane. 5 contained 97.5 D_1 and 2.5% D_0 species.

Diethyl-(2-phenylpropyl)malonate¹⁰ (8) was prepared from the tosylate 6 by a known method¹¹ in a 64% yield; b.p. 125-130 °C/0.2 Torr; $n_D^{20} = 1.4850$. Mass spectrum: 278 ([M]⁺⁻), 233, 187, 160 (base peak), 133, 118, 105, 88.

Diethyl-(2-[D₁]-2-phenylpropyl)malonate (9) was prepared from the tosylate **7**. **9** contained 97.3 ${}^{2}D_{1}$ and 2.7 D₀ species. $n_{D}{}^{20} = 1.4846$; Mass spectrum: 279 ([M]⁺⁻), 234, 188, 161 (base peak), 160, 134, 133, 118, 106, 89.

4-Phenylvaleric acid¹² (10) was prepared by hydrolysis/decarboxylation of **8** (Ref. 13). B.p. 128–133 °C/0.1 Torr; $n_D^{20} = 1.5119$.

(4-[D₁])-4-Phenylvaleric acid (11) was prepared from 9 as described for 10. 11 contained $97.2 D_1$ and 2.8% D_0 species.

1,4-Diphenyl-1-pentanone (12)

The acid 10 (1.6 g, 9 mmol) was converted to its lithium salt by refluxing with lithium hydride (80 mg, 10 mmol) in tetrahydrofuran (10 cm^3) for 2 h. The solution was cooled to 0 °C and a solution of phenyllithium (11 mmol) in ether (15 cm³) was added dropwise under argon. The reaction mixture was stirred at 20 °C for 4 h and then quenched by pouring into dilute hydrochloric acid. The product was extracted with ether, the extract was washed with 5% sodium carbonate, dried over sodium sulphate and ether was evaporated in vacuo. Chromatography on silica gel (chloroform-hexane) and distillation at 180 °C /0.1 Torr (bath temperature) afforded 1.9 g (89%) of 12 as a viscous oil. Found: C. 85.80; H, 7.65. Calc. for C₁₇H₁₈O: C, 85.67; H, 7.61%. Mass spectrum: 238 ([M]^{+·}), 220, 120 (base peak), 118, 105, 77.

(4-[D₁])-1,4-Diphenyl-1-pentanone (13)

The ketone **13** was prepared from **11** as described for **12**. **13** contained 95.6% D_1 and 4.4% D_0 species. Mass spectrum: 239 ([M]⁺⁻), 221, 121 (base peak), 120, 118, 106, 105, 77.

1-[D₅]Phenyl-4-phenyl-1-pentanone (14)

14 was prepared from **10** by using $[D_5]$ phenyllithium (generated from $[D_5]$ bromobenzene and lithium powder in ether). **14** contained 88.9% D_5 and 11.1% D_4 species. Mass spectrum; 243 ($[M]^{+-}$), 225, 125 (base peak), 118, 110, 109, 105, 82. IR (film): 2277. 1947, 1873, 1806, 1727, 1684, 1603, 1565, 1497. 1453, 1410, 1387, 1333, 1297, 1253, 1210, 1171, 1046, 1017, 973, 965, 910, 835, 827, 767, 705, 633, 542, 527 cm⁻¹.

(2,2-[D₂])-1,4-Diphenyl-1-pentanone (15)

Ketone **12** (400 mg) and decyl trimethylammonium bromide (30 mg) in tetrahydrofuran (5 cm³) were stir-

red with 6 cm³ of deuterium oxide containing 40 mg of lithium deuteroxide. After stirring for 40 h at 20 °C, dry ice (500 mg) was added to the mixture, the aqueous phase was saturated with sodium sulphate and the product was taken up with pentane-chloroform. The crude ketone **15**, obtained after evaporating the solvents, gave a single spot in thin-layer chromatography and it was used without further purification. **15** contained 88.8% D_2 and 11.2% D_1 species.

(2,2,4-[D₃])-1,4-Diphenyl-1-pentanone (16) was prepared from 13 as described for 15. Deuterium content: 91.0% D₃; 9.0% D₂ Mass spectrum: 241 ($[M]^+$), 223, 222, 123, 122, 118, 106, 105, 77.

2,5-Diphenyl-1-hexene (1)

Ketone 12 (1.2 g, 5 mmol) in tetrahydrofuran (5 cm³) was added to a stirred solution of triphenylmethylphosphorane (7.5 mmol) in ether at 0 °C under argon. After 2 h at 20 °C the reaction mixture was quenched with water, the ethereal solution was washed with brine, dried, and the solvent was evaporated in vacuo. Chromatography (silica gel, hexane-chloroform, 8:3) followed by distillation at 130-140 °C at 0.2 Torr (bath temperature) afforded 950 mg (80%) of 1: $n_D^{20} = 1.5662, n_D^{25} = 1.5646$ (Ref. 16 gives $n_D^{25} =$ 1.5652). IR (film): 3083, 3060, 3027, 3000, 1945, 1875, 1802, 1748, 1630, 1606, 1577, 1500, 1457, 1380, 1033, 900, 785, 770, 707, 540 cm⁻¹. ¹H NMR(CDCl₃): 1.20d (J = 11.8 Hz), 3H; 1.47-1.92 m, 2H; 2.15–2.95 m, 3H; 4.98dd (J = 2.5 Hz,4.9 Hz), 1H; 5.23d (J = 2.5 Hz), 1H; 7.20 m, 5H; 7.27 m. 5H.

(3,3-[D₂])-2,5-Diphenyl-1-hexene (2) was prepared from 15 as described for 1. 2: $n_D^{20} = 1.5652$; IR (film): 3083, 3060, 3027, 3000, 2207, 2197, 2106, 1945, 1875, 1800, 1747, 1620, 1597, 1570, 1490, 1447, 1440, 1370, 1075, 1023, 900, 776, 760, 697, 544 cm⁻¹; ¹H NMR(CDCl₃): 1.22d (J = 11.7 Hz), 3H; 1.72d (J = 11.7 Hz), 2H; 2.70 m, 1H; 5.00d (J =2.6 Hz), 0.9 H; 5.23d (J = 2.6 Hz), 0.7H; 7.20 m, 5H; 7.27 m, 5H. Quenching the reaction mixture with deuterium oxide resulted in a partial incorporation of deuterium at C-1 (cf. Table 1).

2-[D₅]Phenyl-5-phenyl-1-hexene (3) was prepared from **14** as described for **1**. **3**: $n_D^{20} = 1.5654$; Ir (film): 3083, 3060, 3027, 3000, 2273, 1945, 1875, 1802, 1745, 1628, 1606, 1495, 1455, 1380, 1324, 1033, 896, 840, 770, 705, 545 cm⁻¹; ¹H NMR (CDCl₃): 1.20d (J = 11.8 Hz), 3H; 1.47–1.92 m, 2H; 2.15–2.95 m, 3H; 4.98dd (J = 2.3 Hz, 4.9 Hz), 1H; 5.33d (J = 2.5 Hz), 1H; 7.20 m, 5.2H.

(3,3,5-[D₃])-2,5-Diphenyl-1-hexene (4) was prepared from 16 as described for 1. The reaction mixture was quenched with deuterium oxide which resulted in incorporation of some deuterium at C-1 (cf. Table 1). 4: $n_D^{20} = 1.5658$; IR (film): 3080, 3057, 3023, 2200, 2115, 1942, 1873, 1803, 1747, 1622, 1600, 1572, 1493, 1447, 1373, 1320, 1277, 1183, 1157, 1100, 1075, 1030, 900, 849, 763, 705, 540 cm^{-1} ; ¹H NMR(CDCl₃): 1.22 s, 3H; 1.70t, 2H; 5.00d (J = 2.7 Hz), 0.56H; 5.23d (J = 2.7 Hz) 0.65H; 7.20 m, 5H; 7.27 m, 5H.

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