# On the Generation and Characterization of the Spiro[2,5]octadienyl Anion in the Gas Phase<sup>†‡</sup>

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Three routes have been explored in both a high-pressure chemical ionization (CI) source and a low-pressure Fourier transform ion cyclotron resonance (FT-ICR) cell to generate the spiro[2,5]octadienyl anion in the gas phase: (i) proton abstraction from spiro[2,5]octa-4,6-diene; (ii) expulsion of trimethysilyl fluoride by phenyl ring participation following fluoride anion attack upon the silicon centre of 2-phenylethyl trimethylsilane; and (iii) collisionally induced dissociation (CID) of the carboxylate anion of 3-phenylpropanoic acid via carbon dioxide loss. From comparison of the CID spectra of various reference  $[C_8H_9]^-$  ions with those of the  $[C_8H_9]^-$  ions which could be generated via the routes (i) and (iii) in the CI source it can be concluded that only the third route yields a  $[C_{\bullet}H_{o}]^{-1}$ ion whose CID spectrum is not inconsistent with the one expected for the spiro[2,5]octadienyl anion. In the FT-ICR cell  $[C_8H_9]^-$  ions are generated along all three routes; their structures have been identified by specific ion-molecule reactions and appear to be different. Route (i) yields an *a*-methyl benzyl anion, probably due to isomerization within the ion-molecule complex formed. An ortho-ethylphenyl anion is formed along route (ii), presumably due to an intramolecular ortho proton abstraction in the generated trimethylsilyl fluoride solvated 2-phenylethyl primary carbanion. The [C8H9] ion formed along route (iii) shows reactions similar to those of the 1,1dimethylcyclohexadienyl anion which is structurally related to the spiro[2,5]octadienyl anion. Furthermore, the  $[C_8H_9]^-$  ion generated via route (iii) reacts with hexafluorobenzene under expulsion of only one hydrogen fluoride molecule which contains exclusively one of the original phenyl ring hydrogen atoms. On the basis of all these observations it is therefore quite likely that the spiro[2,5]octadienyl anion is formed by collisionally induced decarboxylation of the 3-phenylpropanoic acid carboxylate anion and can be a long-lived and stable species in the gas phase.

### INTRODUCTION

More than a decade ago one of  $us^1$  showed, on the basis of collisionally induced dissociation (CID) and stable isotopic labelling experiments, that the ethylenebenzenium or 'phenonium' ion (*a*) can be a long-lived species in the gas phase.<sup>2</sup>



Since then various methods in mass spectrometry have been developed and improved to generate and detect anions in the gas phase and to elucidate their structures.<sup>3</sup> This prompted us to make an attempt at preparing and characterizing the negative counterpart of ion *a*, i.e., the spiro[2,5]octadienyl anion (b),<sup>4</sup> in the gas phase.

The anion b, or substituted analogues, in the condensed phase have received considerable interest. For example, early mechanistic studies of 1,2-aryl shifts in

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carbanions showed a significant preference of a 1,2phenyl shift over a 1,2-tolyl shift. This observation was considered to point at the intermediacy of a carbanion such as b, which is supposed to be more stable than the analogous tolyl derived carbanion structure.<sup>4</sup> However, in spite of extensive experimentations the anion structure b could neither be detected by NMR spectroscopy nor be trapped via specific chemical reactions.<sup>5</sup> On the other hand, the approach to increase the stability of anion b by an electron push-pull mechanism, i.e. via methyl substitution of the cyclopropane moiety and phenyl substitution of the cyclohexadienyl anion moiety in the 6-position, and consequently the possibility to trap it, was more successful. Thus, 1,1,2,2-tetramethyl-6phenylspiro[2,5]octa-4,7-diene-6-carboxylic acid (1) was formed after carbonation of the reaction solution of Eqn (1)<sup>5(b)</sup> This result points to a caesium cation-1,1,2,2,-tetramethyl-6-phenylspiro[2,5]octadienyl anion complex (c) in solution, as carbonation is believed to trap anion intermediates with a finite lifetime.



However, it cannot be excluded that the the above mentioned 1,2-aryl shifts take place via a radical mechanism

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and that actually a radical is trapped in the carbonation reaction.<sup>6</sup> It will be clear that in solution chemistry the anion vs. radical mechanism may continue to be a matter of debate as long as counterion and solvation effects thwart the detection of b, which is not the case in gas-phase ion chemistry where, in the absence of counterions or solvent molecules, only isolated ions are detected.<sup>3(b)</sup>

The cyclopropane ring closed anion of interest (b), however, could well be a stable species in the gas phase. The cyclohexadienyl anion itself is known to be stable in the gas phase, its corresponding radical being estimated to have an electron affinity of  $56 \pm 40$  kJ/mol.<sup>7</sup> A very early LCAO-MO calculation has indicated that the possible cyclopropane ring opening of b to form the 2-phenylethyl primary carbanion d would be slightly endothermic,<sup>4</sup> but to our knowledge further information on the interaction between the cyclopropane and the cyclohexadienyl anion moieties in anion b is not available.



In this article the results of experiments to generate and characterize the spiro [2,5] octadienyl anion (b) in the gas phase will be reported.

## EXPERIMENTAL

## Mass spectrometric measurements

For the anion generation under relatively high pressure negative ion chemical ionization (NICI) conditions and the anion structure elucidation by collisionally induced dissociation (CID)<sup>8</sup> a VG Micromass ZAB-2HF mass spectrometer<sup>9</sup> of reversed geometry (BE) was used. All spectra were recorded with a VG 11-250 data system.

Typical NICI conditions were: source temperature 280 °C, repeller voltage 0 V, emission current 5 mA, electron energy 100–250 eV and ion gauge indicated source pressure  $\approx 4 \times 10^{-4}$  Pa.

The neutral compounds were introduced via a heated septum inlet ( $\approx 190$  °C). A small amount of water to generate OH<sup>-</sup> as base was also introduced. The elemental composition of the precursor anions was checked under high-resolution conditions (10 000 at 10% valley).

Apart from the signals of the  $[C_8H_9]^-$  ions and their deuterated analogues formed from undeuterated and deuterated 3-phenylpropanoic acid ethyl esters, respectively, all  $[C_8H_9CO_2]^-$  and  $[C_8H_9]^-$  ion signals had intensities which were at least two orders of magnitude larger than the background noise.

For the  $[C_8H_9]^-$  ions formed by proton abstraction from the  $C_8H_{10}$  precursor hydrocarbons, the m/z = 105  $([C_8H_9]^-)$  signal was the most intense signal in the NICI spectrum apart from the signal due to OH<sup>-</sup>.

In the NICI spectra of the used ethyl esters the most intense signals were due to the  $[M - H]^-$  and the carboxylate  $[M - C_2H_5]^-$  ions (ratio  $\approx 1$ ), while those due to  $[C_8H_9]^-$  ions were small (relative intensity 1–15%).

The anions were accelerated through a potential of 8 kV and subsequently mass selected. CID was achieved by passing these anions through a collision cell in the second field-free region filled with the target gas (helium) at such pressure that the intensity of the main beam was reduced to 50% of its original value. This corresponded to a pressure of  $\sim 10^{-5}$  Pa at the ion gauge reading above the corresponding pump.

To improve the signal-to-noise ratio, the CID spectra presented in this article were accumulated; ~20 scans for the 3-phenylpropanoic acid carboxylate anions and up to ~100 scans for the  $[C_8H_9]^-$  ions. The yield of daughter carbanions generated by CID from the  $[C_8H_9]^-$  precursor ions was low as can be seen in Table 1 (vide infra).

Anion generation under low-pressure conditions and ion structure elucidation by specific ion-molecule reactions were performed on a home-built FT-ICR mass spectrometer described in detail elsewhere.<sup>10</sup>

All anions were trapped in the cubic FT-ICR cell (15.6 cm<sup>3</sup>) at a magnetic field of 1.4 T by application of a small negative potential (-2.5 V) to the trapping plates. Electrons were continuously removed from the cell by excitation of their harmonic oscillations along the axis of the magnetic field by applying an approximately 8 MHz signal to the trapping plates.<sup>11</sup>

Precursor anions were made along dissociative electron attachment or proton abstraction routes;  $OH^-$  from  $H_2O$ ,  $NH_2^-$  from  $NH_3$ ,  $O^-$  from  $N_2O$ ,  $CH_3O^-$  from  $CH_3OH$  or  $CH_3ONO$ , and  $F^-$  from  $CF_4$  (typical pressures =  $4 \times 10^{-5}$  Pa). Following their generation by an electron-beam pulse of relatively long duration (40 ms) to improve the signal-to-noise ratios of the signals due to the end product anions, these anions were isolated in the cell and all other anions removed from the cell by creation of a notch in the waveform of a relatively slow excitation pulse (scan speed 68 kHz ms<sup>-1</sup>).<sup>12</sup> Subsequently, they were allowed to react for about 200 ms with the neutral compound (typical pressures =  $4 \times 10^{-5}$  Pa) to form the anion of interest, which then was isolated in the cell.

In this way carboxylate anions were generated by the reaction of O<sup>-•</sup> with the corresponding carboxylic acid ethyl esters (typical pressures  $= 4 \times 10^{-5}$  Pa). The <sup>18</sup>O-carboxylate anion of 3-phenylpropanoic acid was formed by a B<sub>AC</sub>2-reaction of <sup>18</sup>O<sup>-•</sup> generated from N<sub>2</sub><sup>18</sup>O with the corresponding ethyl ester.<sup>13</sup>

The formed and isolated carboxylate anions were then decarboxylated by low-energy CID<sup>14</sup> with N<sub>2</sub>O as collision gas (typical pressure =4 × 10<sup>-5</sup> Pa) to give the desired  $[C_8H_9]^-$  ions. A short, but intense, radiofrequency pulse at the cyclotron frequency of the anions was used (0.02 ms duration, 10 V peak-to-peak) to excite the carboxylate anions translationally up to a (calculated) translational energy of ~100 eV. The  $[C_8H_9]^-$  ions were also formed when argon or H<sub>2</sub>O were used as collision gases. After the CID a relatively short delay time (50 ms) was applied before isolating the  $[C_8H_9]^{-1}$  ions in the cell to probe their structure by specific ion-molecule reactions.

Abundant  $[C_8H_9]^-$  ions were formed as in Eqn (2) (vide infra), while reactions as represented by Eqns (3) and (4) (vide infra) gave rise to small, but detectable signals due to  $[C_8H_9]^-$  ions with signal-to-noise ratios of ~ 50.

The  $[C_8H_9]^-$  ions were allowed to react for ~1000 ms following their isolation in the cell with neutral compounds added to the system (typical pressure =  $3 \times 10^{-5}$  Pa) to probe their structure.

The signal-to-noise ratio of the FT-ICR spectra thus obtained was improved by signal averaging via accumulation of 200 to 1000 transients prior to Fourier transformation.

#### Materials

Spiro[2,5]octa-4,6-diene (2) was generated as described in the literature<sup>15</sup> from spiro[2,5]octa-5-ene, which was a generous gift from Prof. Dr A de Meijere of the University of Hamburg.

1,1-Dimethylcyclohexa-1,3-diene was generated via the same route from commercially available 1,1-dimethylcyclohex-2-ene.<sup>16</sup>

2-Phenylethyl trimethylsilane (3) and its deuterated analogues were synthesized from 2-phenylethyl bromide and its deuterated analogues, respectively, as described by Seyferth *et al.*<sup>17</sup>

The 3-phenylpropanoic acids and the *ortho*- and *para*-ethylbenzoic acids were obtained by carbonation of the Grignard complexes of the 2-phenylethyl and the *ortho*- and *para*-ethylphenyl bromides, respectively.<sup>18</sup>

1,1- $d_2$ -2-Phenylethyl bromide was synthesized by a successive H/D-exchange of the sodium salt of phenylacetic acid (three times) in a basic D<sub>2</sub>O/NaOD solution (pH  $\approx$ 13), lithium aluminium hydride reduction of the H/D-exchanged acid and bromination with phosphorus tribromide of the alcohol formed. 2,2- $d_2$ -2-Phenylethyl bromide was synthesized by lithium aluminium deuteride reduction of phenylacetic acid and bromination with phosphorus tribromide of the alcohol formed.

2-Pentadeuterophenylethyl bromide was synthesized by the addition of ethylene oxide to  $d_5$ -phenyl- magnesium bromide and bromination with phosphorus tribromide of the alcohol formed.

The  $d_2$ - and  $d_5$ -label contents of the synthesized 2phenylethyl bromides described were determined by 70 eV electron impact mass spectrometry to be >98%, which did not change upon conversion of the bromides into the corresponding 2-phenylethyl trimethylsilanes and 3-phenylpropanoic acids (vide supra). Esterfication of the carboxylic acids to the ethyl esters was achieved by standard methods.<sup>18</sup>

Cyclooctratriene<sup>19</sup> and  $CH_3ONO^{20}$  were synthesized as described in the literature. The 7-methylcycloheptatriene was available in our laboratory. The other compounds used were commercially available.<sup>16</sup>

All compounds were purified by preparative gas chromatography using a 15% OV 17 column at 20 °C to 210 °C and all synthesized compounds were checked by mass spectrometry and <sup>1</sup>H-NMR with regard to composition, structure and label content.

#### **RESULTS AND DISCUSSION**

Three different routes for the generation of the spiro[2, 5] octadienyl anion (b) have been tested in both a highpressure chemical ionization source  $^{3(e)}$  of a sector mass spectrometer of reversed geometry<sup>8</sup> and a low-pressure Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer.<sup>21</sup> The three different routes are as follows.

(i) Proton abstraction from spiro[2,5]octa-4,6-diene (2). This reaction, in principle, should yield anion b as shown in Eqn (2), provided that the gas-phase anion B<sup>-</sup> is sufficiently basic.

(ii) Nucleophilic displacement reaction by attack of a fluoride anion upon 2-phenylethyl trimethylsilane (3). Stable carbanions can be generated by a nucleophilic displacement reaction at silicon centres via a pentacoordinated silicon anion complex as shown by DePuy *et al.*<sup>22</sup> and Bowie and co-workers.<sup>23</sup>

On this basis it was reasoned that the pentacoordinated silicon anion complex formed by attack of  $F^$ upon 2-phenylethyl trimethylsilane (3) might break up either directly into the desired anion b or into the primary 2-phenylethyl anion (d) and trimethysilyl fluoride as shown in Eqn (3).



Usually gas-phase primary carbanions have a negative or vanishingly small electron affinity<sup>24</sup>† and are therefore rare. However, analogous to the stabilization of primary carbanions in the condensed phase by appropriate solvent molecules, the 2-phenylethyl anion (d) might be stabilized in the presence of trimethysilyl fluoride thereby increasing the possibility of ring closure to the desired anion b vs. electron detachment (Eqn (3)).

(iii) Decarboxylation of an excited 3-phenylpropanoic acid carboxylate anion e. Graul and Squires have shown recently that stable carbanions which are not accessible by conventional ionization methods can be formed by (endothermic) collisionally induced decarboxylation of the corresponding carboxylate anions.<sup>25</sup> Such a reaction in an excited 3-phenylpropanoic acid carboxylate anion (e) might lead to the formation of the desired anion (b) if the decarboxylation is accompanied by ring closure as shown in Eqn (4).

<sup>†</sup> The gas-phase electron affinity, EA, of a neutral species is defined as the negative of the enthalpy change of the reaction  $A + e \rightarrow A^{-1}$ .



In the discussion below the results obtained with the sector mass spectrometer will be presented first.

# Anion generation at high pressure and structure elucidation by CID

 $[C_8H_9]^-$  ions are generated from spiro[2,5]octa-4,6diene (2) in the CI ion source by the deprotonation reaction as given in Eqn (2) and confirmed by accurate mass measurements (m/z (measured) 105.069 dalton; m/z(calcd) 105.070 dalton). However, the aimed nucleophilic displacement reaction by attack of the fluoride anion upon 2-phenylethyl trimethylsilane (3) (Eqn (3)) does not lead, with the experimental set-up used, to a  $[C_8H_9]^-$  ion signal of reasonable intensity. Carboxylate anions of 3-phenylpropanoic acid (e) i.e. the precursor anions for the decarboxylation reaction given by Eqn (4), are formed from the ethyl ester of 3phenylpropanoic acid in the CI source. However, the route of their formation, which could be  $S_N 2$  substitution,<sup>26</sup> base-induced elimination<sup>26</sup> or dissociative electron attachment,<sup>27</sup> is not precisely known.

The (high-energy) CID spectra of the isotopically labelled 3-phenylpropanoic acid carboxylate anions, generated from the specifically labelled esters, are given in Fig. 1. The mass shift of the main product anion as a function of the label content proves that  $[C_8H_9]^-$  ions are the main product anions of collisionally excited 3phenylpropanoic acid carboxylate anions (e).

 $[C_8H_9]^-$  ions are also generated in the CI source from the ethyl ester of 3-phenylpropanoic acid, albeit in a small amount. They presumably arise from excited 3phenylpropanoic acid carboxylate anions (e) (m/z (measured) 105.072 dalton; m/z (calcd) 105.070 dalton;  $[C_8H_9]^- \approx 1\%$  of  $[C_8H_9CO_2]^-$ ). In this case a small signal due to a  $[C_7H_5O]^-$  ion (m/z (measured) 105.035



**Figure 1.** High-energy CID spectra (ZAB-2HF) of (a)  $[C_6H_5C_2H_4CO_2]^-$  (m/z = 149), (b)  $[C_6H_5CD_2CH_2CO_2]^-$  (m/z = 151) (c)  $[C_6H_5CH_2CD_2CO_2]^-$  (m/z = 151), and (d)  $[C_6D_5C_2H_4CO_2]^-$  (m/z = 154), anions, generated from the corresponding specifically labelled ethyl esters of 3-phenylpropanoic acid, respectively.

dalton; m/z (calcd) 105.034 dalton,  $[C_7H_5O]^- \approx 10\%$  of  $[C_8H_9]^-$ , which is also formed upon CID (see Fig. 1), is detected as well.

The reference  $[C_8H_9]^-$  ions, i.e. the  $\alpha$ -methylbenzyl anion (f), the cyclooctatrienyl anion (g), the 7methylcycloheptatrienyl anion (h) and the *ortho*- and *para*-ethylphenyl anions (i) and (j) are generated in the CI source by proton abstraction from ethylbenzene, cyclooctatriene and 7-methylcycloheptatriene<sup>31(d)</sup> and by base-induced elimination/decarboxylation reactions on the ethyl esters of *ortho*- and *para*-ethylbenzoic acid, respectively.



In Table 1 the relative abundances of the CID product anions of the  $[C_8H_9]^-$  ions, generated from

spiro[2,5]octa-4,6-diene (2) and the ethyl ester of 3phenylpropanoic acid, and of the reference  $[C_8H_9]^$ ions f to j are given. In addition, partial CID spectra of some of the  $[C_8H_9]^-$  ions are presented in Fig. 2.

In the case of the  $[C_8H_9]^-$  ion formed from the ethyl ester of 3-phenylpropanoic acid the signal due to the  $[C_7H_5O]^-$  ion (vide supra) may disturb the CID spectrum of the  $[C_8H_9]^-$  ion. However, the HCO radical loss from the  $[C_7H_5O]^-$  ion, generated by deprotonation of benzaldehyde, to form the  $[C_6H_4]^-$  radical ion (m/z = 76) is not so pronounced in the CID spectrum of the  $[C_8H_9]^-$  ion, if it is due to that reaction at all (see Table 1). Moreover, the signal due to hydrogen atom loss (m/z = 104) in the  $[C_8H_9]^-$  ion CID spectrum is also considerably more intense than expected from the  $[C_7H_5O]^-$  ion as can be seen from the data in Table 1. It is believed therefore that the major part of the CID product anions of m/z = 105 from the ethyl ester of 3phenylpropanoic acid can be attributed to the hydrocarbon  $[C_8H_9]^-$  ion structure. Comparison of the data in Table 1 shows that the  $[C_8H_9]^-$  ions generated from both spiro[2,5]octa-4,6-diene (2) and the ethyl ester of

Table 1. Relative abundances of the product anions of high-energy CID (ZAB-2HF) of the  $[C_8H_9]^-$  ions (m/z = 105) generated from spiro[2,5]octa-4,6-diene (2), the ethyl ester of 3-phenylpropanoic acid, ethylbenzene, the ethyl esters of ortho- and para-ethylbenzoic acid, cyclooctatriene and 7-methylcycloheptatriene and the  $[C_7H_5O]^-$  ion generated from benzaldehyde, respectively. Abundances (from peak heights) are given with respect to the most intense signal with a m/z value smaller than 104. The experimental error is ~25% due to the low signal-to-noise ratios

				Relative abundances of ions with the following $m/z$ values														
		Reference anion																
Eqn.	Compounds	structure		Fig.	25	26	27	39	64	65	76	77	79	89	90	103	104	105
(2)	Š			2(a)	2	25	2		5	5		100	3		15		1100	10 <sup>5</sup>
(4)				2(b)	<5		<5				<5	100	<5		<5		400	10 <sup>5</sup>
	$\bigcirc$		f	2(c)	5	5					20	100	<5		90	5	100	10 <sup>5</sup>
		<b>S</b>	i	2(d)	<5				<5	<5		100			10		400	10 <sup>5</sup>
		<b>O</b>	j	2(e)	7	4					80	30			100	70	500	2 × 10 <sup>5</sup>
	$\bigcirc$	$\bigcirc$	g		3		100		5	5		10	8	6	4	100	250	5 × 10 <sup>5</sup>
	$\bigcirc$	Ó	h		44		17	10		23		27	100			60	250	10 <sup>6</sup>
	Ø		a		<1						10	100					20	10⁴
<sup>a</sup> All the	protons in benzaldehy	de are known	to b	oe near	ly equ	ially a	acidic,	<sup>37</sup> the	[C,F	l²0]_	ions	formed	thus	hav	e diffe	rent sti	ructures	s.



**Figure 2.** Partial high-energy CID spectra (ZAB-2HF) of  $[C_8H_9]^-$  ions (m/z = 105) formed from (a) spiro[2,5]octa-4,6-diene (2), (b) the ethyl ester of 3-phenylpropanoic acid, (c) ethylbenzene, and the ethyl esters of (d) *ortho-* and (e) *para-* ethylbenzoic acid, respectively (The 'm/z = 84 and 85' signals in the spectra of (a)–(d) originate from first field-free region decompositions detected due to the low resolution conditions applied<sup>8</sup>). The signal between m/z = 88 and m/z = 92 in (b) is magnified by a factor of 10.

ortho-ethylbenzoic acid suffer upon CID from an abundant ethene (m/z = 77) and a minor methyl radical loss (m/z = 90), but they differ significantly in the production of m/z = 26. The  $[C_8H_9]^-$  ions formed from the ethyl ester of 3-phenylpropanoic acid show practically only ethene loss upon CID.

These three CID spectra, however, do differ significantly from those of the reference  $[C_8H_9]^-$  ions f, g, h and j.

The anion structure b is expected to decompose mainly by ethene loss under formation of the phenyl anion (m/z = 77) (Eqn (5)). A cyclopropane ring opening of b will give anion d whose corresponding radical has been estimated to have a vanishingly small electron affinity of  $0 \pm 13$  kJ/mol.<sup>28</sup><sup>‡</sup> It is therefore expected

<sup>&</sup>lt;sup>‡</sup> The given electron affinity for the corresponding radical of the 2-ethylphenyl primary carbanion (d) of  $0 \pm 13 \text{ kJ/mol}^{-1}$  is calculated from the known carbon-hydrogen bond strength<sup>28(a)</sup> and the measured proton affinity of 1699  $\pm$  13 kJ/mol. The latter was determined from the measured ratio of  $2.6 \pm 0.2$  of ethylbenzene and methane loss from the ion-molecule complex of 2-phenylethyl trimethylsilane (3) and the hydroxide anion in correlation with the relationship between product ratio and proton affinity as given by De Puy *et al.*<sup>28(b)</sup>

that anion d will be unstable with respect to electron detachment. However, if this anion would have such a lifetime that an *ortho*-proton abstraction can take place prior to electron detachment, an anion with an *ortho*-ethylphenyl anion structure (i) may be formed which subsequently may lose to a minor extent a methyl radical (m/z = 90) (Eqns (5) and (6)). Because the anion i itself also decomposes mainly via an intramolecular base-induced ethene elimination (see Fig. 2(d) and Eqn (6)) this would not facilitate a clear distinction between anions b and i by CID.



However, even if such an isomerization of b to i via ddoes occur, a difference in the ratio between the ethene loss (m/z = 77) and the methyl radical loss (m/z = 90)may be expected for anions b and i in such a sense that the former should show a less abundant methyl loss. Such a difference is indeed found in the spectra shown in Figs 2(b) and (d), but not in those shown in Figs 2(a) and (d), which leads to the supposition than anion bmight have been formed via Eqn (4) but not via Eqn (2). Support for the supposition that the spiro[2,5]octadienyl anion structure would be formed by decarboxylation of 3-phenylpropanoic acid carboxylate anions could be gained if the CID spectra of the  $[C_8H_7D_2]^$ ions (m/z = 107) formed from the ethyl esters of 2,2- and  $3,3-d_2$ -labelled 3-phenylpropanoic acid proved to be equal. Unfortunately, the CID spectra of these anions gave ambiguous results.

In the CID spectrum of the  $[C_8H_4D_5]^-$  ion (m/z = 110) formed from the ethyl ester of the  $d_5$ -phenyl ring labelled 3-phenyl propanic acid, however, a clear m/z = 82 signal is found.

As shown recently,<sup>29</sup> collisionally induced removal of two electrons from anions known as charge reversal (CR)<sup>30</sup> could be a structure probe to distinguish some different isomeric  $[C_8H_9]^-$  ions. Unfortunately, the CR-spectra turned out to be nearly identical for all the generated  $[C_8H_9]^-$  isomeric ions mentioned in this work.

The results presented in this section permit us to draw the conclusion that  $[C_8H_9]^-$  ions can be formed along the routes given by Eqn (2) and Eqn (4) under high pressure conditions. Their CID spectra are clearly distinct from those of nearly all other  $[C_8H_9]^-$  ion

structures. The negligible, if any, methyl loss from  $[C_8H_9]^-$  ions formed along the route of Eqn (4) (see Fig. 2(b)) and the shift of the signal at m/z = 77 to m/z = 82 upon complete deuteration of the phenyl ring suggests that b is formed via reaction (4).

To support this further,  $[C_8H_9]^-$  ions have been generated and studied by ion-molecule reactions in a Fourier transform ion cyclotron resonance mass spectrometer as discussed in the following section.

#### Anion generation at low pressure and structure elucidation by specific ion-molecule reactions

The results of generation of  $[C_8H_9]^-$  ions along the routes given by Eqns (2), (3) and (4) from unlabelled and labelled compounds and of some reference anions are given in Table 2. The decarboxylation of the carboxylate anions according to Eqn (4) is achieved by low-energy CID.

The  $C_8H_9$  composition of the anions formed via the reactions (2) and (3) has been checked by accurate mass measurements (Eqn (2): m/z (measured) 105.0702 dalton; Eqn (3): m/z (measured) 105.0728 dalton; m/z (calcd) 105.0704 dalton). The  $C_8H_9$  composition of the anion formed via reaction (3) and also via reaction (4) is further confirmed by the application of specific <sup>2</sup>H and <sup>18</sup>O labelling, see Table 2. Note also from Table 2 that proton abstraction from spiro[2,5]octa-4,6-diene 2 by OD<sup>-</sup> generates not only m/z = 105,  $[C_8H_9]^-$ , but also m/z = 106,  $[C_8H_8D]^-$ , as a consequence of partial H/D exchange in the encounter complex.

Anyhow, it can be concluded firmly that all three routes are effective to generate  $[C_8H_9]^-$  ions under low-pressure conditions.

The reference anions, i.e. the  $\alpha$ -methylbenzyl anion  $f([C_8H_9]^-)$ , the 1,1-dimethyclohexadienyl anion k  $([C_8H_{11}]^-)$  which is supposed to react in the same way as the title anion b owing to their structural relationship, and the *ortho*-ethylphenyl anion i  $([C_8H_9]^-)$  are generated by proton abstraction from ethylbenzene and 1,1-dimethyl-2,4-cyclohexadiene and by low-energy CID of the carboxylate anion of *ortho*-ethylbenzoic acid, respectively.



The following ion-molecule reactions turned out to be appropriate to distinguish the various  $[C_8H_9]^-$  ions and to provide information about their structures, i.e. (i) nucleophilic aromatic addition-elimination reactions of the  $[C_8H_9]^-$  ions with hexafluorobenzene. These lead to structure-diagnostic losses of one or more hydrogen fluoride molecules (Eqn (7)).<sup>32</sup> It should be noted that the  $[C_8H_9]^-$  ions also react by electron transfer to hexafluorobenzene which has a relatively high electron affinity of > 174 kJ/mol.<sup>24</sup>† (ii) Nucleophilic additionelimination reactions of the  $[C_8H_9]^-$  ions with formaldehyde under formation of  $[C_3H_5O]^-$  ions (Eqn (8)).<sup>33</sup>

<sup>&</sup>lt;sup>†</sup> The gas-phase electron affinity, EA, of a neutral species is defined as the negative of the enthalpy change of the reaction  $A + e \rightarrow A^{-1}$ .

Table 2.	Reactivity patterns of [C <sub>8</sub> H <sub>9</sub> ] <sup>-</sup> ions and their deuterated analogues with respect to C <sub>6</sub> F <sub>6</sub> , CH <sub>2</sub> O and CD <sub>2</sub> O (columns 6 to
	8) and $\Delta G_{acid}^0$ values of their conjugated acids (column 9) following generation and isolation of the mentioned ions under
	low-pressure conditions in the FT-ICR cell (columns 1 to 4)

Egn	Compound/ carboxylate anion	Precursor anion/m/z of carboxylate anion	Generated and studied anion	Reference anion structure	Number of HF-losses in C <sub>6</sub> F <sub>6</sub> reaction (eqn 7)	Products of CH <sub>2</sub> O reaction (eqn 8)	Products of CD <sub>2</sub> O reaction	Estimated ΔG <sup>o</sup> <sub>acid</sub> (kJ/mol <sup>−1</sup> )
(2)	$\overline{\frown}$	CH₃O⁻	105		2 HF	ª	Xp	≈1569°
	2	OD-	105		2 HF	—	x	≈1569°
		NH <sub>2</sub> -	105		2 HF/1 HF	x	x	x
	$\widehat{\mathbf{n}}$	CH₃O-	105		2 HF			1561 ± 8ª
(3)	Si(Me), 3	F-	105	~	2 HF	57	58	>1569°
	Day SI(Me)	F⁻	107		2 DF	58	59	x
		F-	107		2 HF	59	60	x
	Si(Me),	F-	110		2 HF	58	59	×
		149	105	O <sub>o</sub> i	2 HF	57	58	≈1632ª
(4)	or the second se	149	105		1 HF		,	<1544° >1527°
		151	107		1 HF	_		x
		151	107		1 HF	x	x	x
		154	110		1 DF	x	×	x
		151	105		x	x	x	x
	$\sim$	CH₃O-	107	(0) ×., k	1 HF	_	x	≈1531ª

<sup>a</sup>'—' indicates that no reaction between the anion of column 4 and the neutral molecule given could be detected under the described experimental conditions. <sup>b</sup>'x' means that the reaction has not been studied. <sup>c</sup> The  $\Delta G^{0}_{acid}$  values have been obtained by 'bracketing' experiments.<sup>31</sup> d The  $\Delta G^{0}_{acid}$  values given have been taken from the literature<sup>31(b)</sup> assuming that those of the conjugate acids of the reference anions *i* and *k* are similar to the  $\Delta G^{0}_{acid}$  values of benzene and cyclohexadiene, respectively.

(iii) Estimates of the gas-phase proton affinities of the different  $[C_8H_9]^-$  ions by gas-phase proton transfer reactions.<sup>31</sup><sup>‡</sup> (iv) The (non)ability of  $[C_8H_9]^-$  ions formed along the route given by Eqn (4) to donate a hydride to strong hydride acceptors (Eqn (9)).<sup>34</sup>

$$C_8H_9^{\textcircled{O}} + C_6F_6 \longrightarrow n HF + C_8H_{(9-n)}C_6F_{(6-n)}^{\textcircled{O}}$$
 (7)

$$C_8H_9 \xrightarrow{\odot} C_3H_5O \xrightarrow{\odot} C_6H_6$$
 (8)

$$C_8H_9^{\bigoplus} + Acc \longrightarrow C_8H_8 + HAcc$$
<sup>(9)</sup>

The results for the first three reactions of the  $[C_8H_9]^-$  ions generated via reactions (2), (3) and (4) and the reference anions are summarized in the last four columns of Table 2. These results allow us to draw the following conclusions. Deprotonation of spiro[2,5]octa-4,6-diene (2) (Eqn (2)) by a base of intermediate proton affinity, such as OH<sup>-</sup> or CH<sub>3</sub>O<sup>-</sup>, yields a  $[C_8H_9]^-$  ion which shows reactions similar to those of the  $\alpha$ -methylbenzyl anion structure *f*. Both anions react with  $C_6F_6$  under expulsion of two HF molecules, but do not react with formaldehyde. In addition, both anions have a gas-phase proton affinity of approximately 1569 kJ/mol. A rationalization of the reaction of anion *f* with  $C_6F_6$ , presumably leading to the formation of a stable substituted fluorenyl anion *l* is given in Eqn (10).

$$\bigcirc \stackrel{\downarrow }{}^{\oplus} \bigcirc \stackrel{\cdot 1 \text{ HF}}{}_{F_{4}} \stackrel{\downarrow }{\longrightarrow} \left[ \bigcirc \stackrel{\downarrow }{}^{\oplus} \bigcirc \stackrel{\cdot 1 \text{ HF}}{}_{F_{4}} \right] \stackrel{\downarrow }{\xrightarrow} \stackrel{\cdot 1 \text{ HF}}{}^{\oplus} \bigcirc \stackrel{\downarrow }{}^{\oplus} \bigcirc \stackrel{\downarrow }{}_{F_{4}} (10)$$

With regard to the methoxy anion it should be noted that although this anion can deprotonate the spiro[2,5] octa-4,6-diene (2) and the  $[C_8H_9]^-$  ion formed can deprotonate methanol, it turned out to be impossible to arrive at such a situation that the gas-phase proton affinity of deprotonated 2 could be determined via an equilibrium.<sup>31</sup> This observation points to an isomerization of the  $[C_8H_9]^-$  ion in such a way that the newly formed anion has a larger proton affinity than the 'original' anion.

Interesting observations are also made if the stronger base  $NH_2^-$  is used to deprotonate the spiro[2,5]octa-4, 6-diene (2). In that case a great drop of the total anion signal intensity and not only the loss of two HF molecules, but also a minor loss of one HF molecule in the reaction of the  $[C_8H_9]^-$  ion formed with  $C_6F_6$  are found (ratio  $\approx 20:1$ ), probably due to the formation of the  $[C_8H_9]^-$  ion in at least two different structures.

Fluoride anion attack on 2-phenylethyl trimethylsilane (3) (Eqn (3)) generates a  $[C_8H_9]^-$  ion whose reactions are similar to those of the *ortho*- ethylphenyl anion structure *i*. Both  $[C_8H_9]^-$  ions react with  $C_6F_6$  under expulsion of two HF molecules and with formaldehyde to form an anion with the composition  $C_3H_5O$ , while both have a proton affinity larger than ~1569 kJ/mol (see Table 2).

The reactions of the  $[C_8H_nD_{9-n}]^-$  (n = 7 and 4) ions, generated from the various labelled 2-phenylethyl trimethylsilanes, with  $C_6F_6$  show that the hydrogen atoms of the eliminated HF molecules exclusively originate from the 2-position. Similarly, the reactions of these anions with formaldehyde show that the product  $[C_3H_5O]^-$  ion contains specifically one hydrogen atom from the phenyl ring, one hydrogen atom from position 2 and two hydrogen atoms from position 1 of the 2phenylethyl trimethylsilanes. The remaining hydrogen atom in the  $[C_3H_5O]^-$  ion stems from formaldehyde itself as proved by reaction with  $CD_2O$  (see Table 2). Note that in the reaction of the reference  $[C_8H_9]^-$  ion *i* with  $CD_2O$  the product anion also contains one deuterium atom (see Table 2).

These observations are rationalized in Eqns (11) and (12), assuming that the  $[C_8H_9]^-$  ion from 2-phenylethyl trimethylsilane has the same structure as the reference  $[C_8H_9]^-$  ion *i*.

It should be noted that the last step in Eqn (12) is identical to the one suggested for the recently reported decomposition of the  $[C_6H_5(C_2H_5)CHO]^-$  ion, generated from  $C_6H_5C^-H(OC_2H_5)$  via a Wittig reaction in the gas phase .<sup>35</sup>



The collisionally induced decarboxylation of the carboxylate anions of 3-phenylpropanoic acid (Eqn (4)) yields a  $[C_8H_9]^-$  ion which, with respect to its chemical reactions shows a great resemblance with the 1,1dimethylcyclohexadienyl anion structure k. Both anions react with  $C_6F_6$  under expulsion of only one HF molecule, do not react with formaldehyde and have a proton affinity of  $\approx 1536$  kJ/mol, but do not transfer a hydride to strong hydride acceptors (vide infra). Eqn (13) rationalizes the reaction between anion k and  $C_6F_6$ .

$$\begin{array}{c} & & \\ & &$$

The hydrogen atom of the HF molecule lost in the reaction of the  $[C_8H_9]^-$  ion, formed along the route given by Eqn (4), with  $C_6F_6$  originates exclusively from

<sup>&</sup>lt;sup>‡</sup> The gas-phase proton affinity of A<sup>-</sup> is defined as the negative of the enthalpy change of the reaction A<sup>-</sup> + H<sup>+</sup> → HA and is indicated as PA (A<sup>-</sup>), being the equivalent to the gas-phase acidity  $\Delta H^0_{acid}$  of acid HA which corresponds to the enthalpy change for the reaction HA → H<sup>+</sup> + A<sup>-</sup>. Gas-phase equilibrium or bracketing measurements yield  $\Delta G^0_{acid}$  values from which  $\Delta H^0_{acid}$  values can be derived by estimation of the entropy change. In this article the  $\Delta G^0_{acid}$  values are given.

the phenyl ring. This observation indicates that the original side-chain carbon atoms do not bear a substantial negative charge in the generated  $[C_8H_9]^-$  ion. This is consistent with the formation of both a spiro[2,5] octadienyl anion b and a bicyclo[4,2,0]octadienyl anion structure m. The latter anion, however, is expected to react with a suitable hydride acceptor by hydride transfer under formation of benzocyclobutane 4 (Eqn (14)). However, the  $[C_8H_9]^-$  ion formed via reaction (4) does neither transfer a hydride ion to formaldehyde nor to carbon dioxide, which have a hydride affinity as high as 172 and 216 kJ/mol, respectively.<sup>34</sup> Apparently the  $[C_8H_9]^-$  ion formed via reaction (4) does not have the structure of the bicyclo[4,2,0]octadienyl anion m.

$$\textcircled{\bigcirc}_{m} + Acc \longrightarrow \textcircled{\bigcirc}_{H} + HAcc \textcircled{\bigcirc}$$
(14)

All the experimental facts taken together therefore provide strong support, if not evidence, that the sought spiro [2,5] octadienyl anion b can be generated by collisionally induced decarboxylation of the 3-phenylpropanoic acid carboxylate anion e and that it can be a stable carbanion in the gas phase.

# Why do the three different routes as given by Eqns (2), (3) and (4) yield $[C_8H_9]^-$ ions with different structures?

An answer to the question why the three different routes, originally supposed to generate  $[C_8H_9]^-$  ions with the same structure *b*, eventually do give  $[C_8H_9]^-$  ions with different structures may be obtained by a qualitative examination of the potential energy surfaces of the reactions.

The abstraction of a proton from the spiro[2,5]octa-4,6-diene (2) by OH<sup>-</sup> (Eqn (2)) to give initially anion b and H<sub>2</sub>O is ~76 kJ/mol exothermic if the  $\Delta G_{acid}^0$  of 2 is taken to be equal to that of cyclohexadiene which has been reported to be 1531 ± 17 kJ/mol.<sup>7(a),31(b),31(c)</sup>

As shown in Fig. 3, under low-pressure conditions this energy, together with the ion-dipole energy due to the electrostatic interaction between the initially generated anion b and  $H_2O$  in the corresponding complex, apparently is sufficient to overcome the unknown barrier of cyclopropane ring opening with concomitant proton abstraction from H<sub>2</sub>O leading to a complex of ethylbenzene and OH<sup>-</sup>. Proton abstraction from the benzylic position of ethylbenzene in this complex eventually leads to the  $[C_8H_9]^-$  ion established to have the  $\alpha$ -methylbenzyl anion (f) structure. The reaction sequence described is estimated to be overall  $\sim 240$ kJ/mol exothermic.<sup>36</sup><sup>†</sup> Note also that partial deuterium incorporation in the generated  $[C_8H_9]^-$  ion (see Table 2) is consistent with the reaction scheme proposed in Fig. 3. This scheme may also shed some light on the observations made if the spiro[2,5]octa-4,6-diene (2) is deprotonated by  $NH_2^{-}$ . In that case the deprotonation step will be  $\approx 50$  kJ/mol more exothermic than with OH<sup>-</sup> as base. This may lead to fast decomposition of a part of the complexes into its components. Depending on the energy distribution between the  $[C_8H_9]^-$  ions and NH<sub>3</sub> species during their separation, the anion structure b thus formed may either suffer from electron detachment as noted from the large drop of the total anion signal intensity or may survive electron detachment as suggested from the expulsion of only one HF molecule in the reaction with  $C_6F_6$  (see Table 2). However, the major part of complexes of initially generated anion b and  $NH_3$  apparently are long-lived enough to generate  $[C_8H_9]^-$  ions in such a structure that two

Table 2). Under high-pressure conditions, reaction (2) does not yield exclusively anion f as can be seen from compari-

HF molecules are eliminated in reaction with  $C_6F_6$  (see

 $\dagger$  Estimated heats of reactions were obtained from the differences in the sums of calculated heats of formation of the initial and final products.<sup>36(a),31(b)</sup> Although a consistent total set of group values for the group additivity of silicon compounds is not available, for the used silicon compounds an estimation could be made from known data.<sup>36(b)</sup>



**Figure 3.** Qualitative potential energy surface for the reaction of OH<sup>-</sup> with spiro[2,5]octa-4,6-diene (2) (Eqn 2).<sup>36</sup> If [CH<sub>3</sub>O]<sup>-</sup> or NH<sub>2</sub><sup>-</sup> is used as base, the exothermicity of the first proton abstraction reaction is  $\approx$  39 kJ/mol and  $\approx$  126 kJ/mol, respectively.



Figure 4. Qualitative potential energy surface for the fluoride anion attack upon 2-phenyl trimethylsilane (3) (Eqn 3).<sup>36</sup>

son of Figs 2(a) and 2(c), i.e. the peak due to the structurally significant methyl loss at m/z = 90 is much smaller in Fig. 2(a) than in Fig. 2(c). In this case presumably most of the initially generated excited ionmolecule complexes of b and the protonated base are stabilized by collisions prior to cyclopropane ring opening, so that a stabilized anion b is formed. Figure 4 shows that in the reaction of the fluoride anion and 2phenylethyl trimethylsilane (3) (Eqn (3)) first a pentacoordinated silicon anion is formed which is expected to be highly excited due to the formation of a strong fluorosilicon bond  $(D(Si-F) \approx 590 \text{ kJ/mol.}^{6(a)}$  This anion could break up in an ion-molecule complex consisting of the 2-phenylethyl primary carbanion d and a trimethylsilyl fluoride molecule, where the latter would stabilize the former with respect to electron detachment. Under these circumstances the anion d can subsequently abstract an ortho proton from the phenyl ring to form eventually the  $[C_8H_9]^-$  ion *i* as indicated by the ion structure determination experiments (vide supra) and trimethylsilyl fluoride as products. The reaction sequence described is estimated to be overall thermoneutral.<sup>36</sup> Support for the 1,4-proton shift in anion d is provided not only by the labelling results for the reactions of labelled  $[C_8H_9]^-$  ions, generated via the route as given in Eqn (3), with formaldehyde and  $C_6F_6$  (vide supra), but also by the previously reported<sup>12(b)</sup> exchange between the ortho and methyl hydrogen atoms of the  $[M - H]^{-}$  ion of methyl phenyl ether prior to loss of formaldehyde. Experimentally the formation of the spiro [2,5] octadienyl anion b and trimethylsilyl fluoride as products from reaction (3) has not been found, which is in line with the estimated 63 kJ/mol endothermicity of this reaction.



**Figure 5.** Qualitative potential energy surface for the collisionally induced decarboxylation of 3-phenylpropanoic acid carboxylate anions (e) (Eqn 4).<sup>36</sup>

The main decomposition path of the pentacoordinated silicon anion, however, corresponds to the formation of deprotonated trimethylsilyl fluoride via a complex of either anion d or anion i and trimethylsilyl fluoride ( $[C_8H_9]^- \approx 5\%$  of  $[SiF(CH_3)_2CH_2]^-$ ). For the collisionally induced decarboxylation of 3-phenylpropanoic acid carboxylate anions (Eqn (4)) the potential energy surface is entered in a totally different way (see Fig. 5). Here stable anions are collisionally excited to a relative broad range of internal energies. The anions which will break up in the 2-phenylethyl anion (d) and carbon dioxide apparently do not survive electron detachment in agreement with the estimated vanishingly small electron affinity of the corresponding radical of anion  $d^{28}$  Probably only those anions which eliminate carbon dioxide by phenyl ring participation, a reaction calculated to be at least 285 kJ/mol endo-

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thermic,<sup>36</sup> can be trapped in a potential energy minimum and thus can lead to the formation of stable anions, which have the structure of the spiro[2,5]octadienyl anion (b).

In conclusion, the present work provides another example that stable anions of low-energy content can be generated by application of the highly endothermic decarboxylation reaction to carboxylate anions.<sup>25</sup>

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