Diagnostic fragmentations of adducts formed between carbanions and carbon disulfide in the gas phase. A joint experimental and theoretical study†

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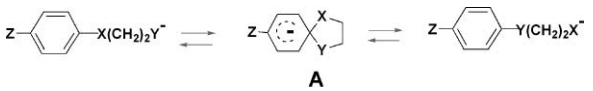
Selected carbanions react with carbon disulfide in a modified LCQ ion trap mass spectrometer to form adducts, which when collisionally activated, decompose by processes which in some cases identify the structures of the original carbanions. For example (i) $C_6H_5^- + CS_2 \rightarrow C_6H_5CS_2^- \rightarrow C_6H_5S^- + CS$, occurs through a 3-membered ring *ipso* transition state, and (ii) the reaction between $C_6H_5CH_2^-$ and CS_2 gives an adduct which loses H_2S, whereas the adduct(s) formed between *o*-$CH_3C_6H_5^-$ and CS_2 loses H_2S and CS. Finally, it is shown that decarboxylation of $C_6H_5CH_2CH_2CO_2^-$ produces the β-phenylethyl anion ($PhCH_2CH_2^-$), and that this thermalized anion reacts with CS_2 to form $C_6H_5CH_2CH_2CS_2^-$ which when energized fragments specifically by the process $C_6H_5CH_2CH_2CS_2^- \rightarrow C_6H_5CH_2^-CHC(S)SH \rightarrow [(C_6H_5CH_2CH{=}C{=}S)\ ^-SH] \rightarrow C_6H_5CH_2CCS^- + H_2S$. Experimental findings of processes (ii) and (iii) were aided by deuterium labelling studies, and all reaction profiles were studied by theoretical calculations at the UCCSD(T)/6-31+G(d,p)//B3LYP/6-31+G(d,p) level of theory unless indicated to the contrary.

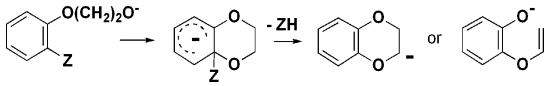
Introduction

A classical (condensed phase) Smiles rearrangement[1] is shown in eqn (1). This nucleophilic *ipso* attack normally requires an electron withdrawing group (*e.g.* nitro, sulfonyl or halogen) either in the *ortho* or *para* position on the aromatic ring; generally X is a good leaving group, Y is a strong nucleophile and Z is shown as a *para* substituent in eqn (1). The anionic Smiles rearrangement has been used extensively synthetically (see *e.g.*[2–9] for some recent examples), and radical Smiles rearrangements have also been reported.[10–14] The Truce–Smiles rearrangement (involving attack of a carbanion centre at an *ipso* electrophilic centre) has also been used as a synthetic method.[15,16]



(1)

The gas phase Smiles rearrangement has not been studied in such depth as that in the condensed phase. The Smiles rearrangement occurs in the gas phase without the necessity for activation of the aromatic ring by electron-withdrawing groups. Heavy atom (^{13}C and ^{18}O) labelling shows that the product ion PhO^- from $PhO(CH_2)_2O^-$ and products PhO^- and PhS^- from $PhS(CH_2)_2O^-$ are formed exclusively from Smiles intermediates **A** (X = Y = O or X = S, Y = O).[17] [For the degenerate process where X = Y = O, calculations at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory indicate that *ipso* intermediate **A** ($\Delta E = +285$ kJ mol^{-1}) is reached *via* a transition state 289 kJ mol^{-1} above $PhO(CH_2)_2O^-$].[18] In contrast, the formation of PhO^- from $PhO(CH_2)_3O^-$ occurs by competitive Smiles (85%) and S_Ni reactions (15%), while PhO^- is formed from $PhO(CH_2)_4O^-$ solely by an S_Ni process.[17] ^{18}O Labelling shows that when there is a substituent in the *ortho* position, the gas phase Smiles rearrangement competes with an *ortho* cyclization process as shown in eqn (2).[19] The classical $[PhNO_2]^{\cdot-}$ to $[PhONO]^{\cdot-}$ gas phase rearrangement is probably an *ipso* process,[20] and gas-phase Smiles processes have been proposed for 2-hydroxybenzyl-*N*-pyrimidinylamine,[21] phenoxy-*N*-phenyl acetamide anions,[22] deprotonated 2-(4,6-dimethoxypyrimidine-2-ylsulfanyl)-*N*-phenylbenzamide[23] and other systems.[24–26]



(2)

We wished to revisit our gas-phase *ipso* rearrangement studies in order to determine whether reactions of CS_2 with aryl carbanions give adducts *cf.*[27,28] which undergo collision-induced cleavages [perhaps *ipso* (Smiles) rearrangements] diagnostic of the structures of the reacting carbanions. The systems we have chosen to react with CS_2 are (a) the phenyl anion, (b) the isomers $PhCH_2^-$ and [*ortho*-$CH_3C_6H_4^-$] and (c) the β-phenylethyl anion ($PhCH_2CH_2^-$) together with some other isomeric anions $C_8H_9^-$. In (c), we wished to determine whether the reaction with CS_2 can settle the old debate[29–31] as to whether the β-phenylethyl anion is stable or

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† Electronic supplementary information (ESI) available: Tables S1 and S1(a): Anion geometries and energies of reaction pathway for the CS_2 addition to the singlet phenyl anion. Tables S2 and S2(a): Anion geometries and energies of reaction pathway for the collision induced dissociation of the singlet $PhCOS^-$ anion. Tables S3 and S3(a): Anion geometries and energies for the possible reaction pathway for the CS_2 addition to the singlet Benzyl anion. Tables S4 and S4(a): Anion geometries and energies of reaction pathway for the interconversion of the singlet anion *o*-$CH_3(C_6H_4)^-$ to singlet $PhCH_2^-$. Tables S5 and S5(a): Anion geometries and energies of reaction pathway for the interconversion of the singlet $PhCH_2CH_2^-$. Tables S6 and S6(a): Potential energy surface for the dissociation of the singlet $PhCH_2CH_2CS_2^-$ anion. Tables S7 and S7(a): Potential energy surface of dissociation of the singlet $PhCH_2CH_2CO_2^-$ anion. See DOI: 10.1039/b916477d

undergoes side chain rearrangement *via* an *ipso*, or some other intermediate.

Results and discussion

1. Reaction of the phenyl anion with CS_2

The phenyl anion was formed in the LCQ mass spectrometer by decarboxylation of the benzoate anion.[32] Reaction of $C_6H_5^-$ with CS_2 forms $C_6H_5CS_2^-$ and collisional activation of this species gives $C_6H_5S^-$ (*m*/*z* 109) as the only observable fragment ion. Reduction in the pressure of the CS_2 reagent gas in this system results in the detection of a minor peak corresponding to *m*/*z* 77 ($C_6H_5^-$) accompanying *m*/*z* 109.

Since anions can react with CS_2 in the gas phase either at C or S,[33] the collision induced negative ion mass spectrum of deprotonated dithiobenzoic acid ($C_6H_5CS_2H$) was measured using a Waters QTOF2 mass spectrometer operating in negative ion electrospray ionization mass spectrometry (ESI MS/MS) mode. We chose the QTOF2 (rather than the LCQ) for this purpose since the QTOF2 uses an efficient gas collision CID MS/MS process for accelerated ions, whereas the LCQ uses a less efficient collisional process in the mass analyser. Two fragment ions, *m*/*z* 77 [($C_6H_5^-$) 100%] and *m*/*z* 109 [($C_6H_5S^-$) 64%] were observed. This is consistent with the adduct of the ion molecule reaction being $C_6H_5CS_2^-$ and suggests that fragment anion $C_6H_5^-$ is produced in the LCQ, but reacts immediately with CS_2 on formation.

In order to compare the reactions of $C_6H_5CS_2^-$ with those of oxygen analogues, we have measured the negative ion CID ESI MS/MS of $[C_6H_5COS]^-$ and $C_6H_5CO_2^-$ using a Waters QTOF2 mass spectrometer. The spectrum of $[C_6H_5COS]^-$ shows *m*/*z* 77 (100%), 93 ($C_6H_5O^-$) 15% and 109 ($C_6H_5S^-$) 55%, while that of the benzoate anion gives *m*/*z* 77 ($C_6H_5^-$) as the only fragment anion. So $C_6H_5CO_2^-$ does not undergo the *ipso* rearrangement, whereas $[C_6H_5COS]^-$ undergoes two competitive *ipso* rearrangements.

The reaction coordinate profiles of the possible *ipso* rearrangements described above have been investigated at the UCCSD(T)/6-31+G(d,p)//B3LYP/6-31+G(d,p) level of theory. All relative energies indicated in the text and in the Figures are ΔG (free energy) values (as requested by a reviewer rather than ΔE). The supplementary tables list both ΔE and ΔG values. Results for the *ipso* processes of $C_6H_5CS_2^-$ and $C_6H_5COS^-$ are summarized in Fig. 1 and 2, with full details of geometries and energies listed in supplementary tables 1 and 2.† No *ipso* intermediates are identified in any case. In the case of $C_6H_5CS_2^-$ (Fig. 1), reaction proceeds through an *ipso* transition state (+316 kJ mol^{-1}) to $[C_6H_5SCS]^-$, which is energized and may decompose to $C_6H_5S^-$ and CS in an overall endothermic reaction (+193 kJ mol^{-1}).‡

The two competitive rearrangements of $[C_6H_5COS]^-$ are shown in Fig. 2. Formation of $C_6H_5S^-$ and CO is endothermic (+26 kJ mol^{-1}) proceeding *via* an *ipso* transition state (+300 kJ mol^{-1}). In comparison, the competitive formation of $C_6H_5O^-$ and CS is more endothermic (+245 kJ mol^{-1}) with a transition state marginally higher in energy (at +306 kJ mol^{-1}).

‡ A reviewer has asked whether electron detachment of the precursor anion competes with the *ipso* rearrangement to form $C_6H_5S^-$. The electron affinity of $C_6H_5CS_2^{\bullet}$ is calculated to be 3.345 eV (332 kJ mol^{-1}) [using the G3B3 level of theory (see Experimental section)] so the process shown in Fig. 1 is more energetically favourable than electron loss.

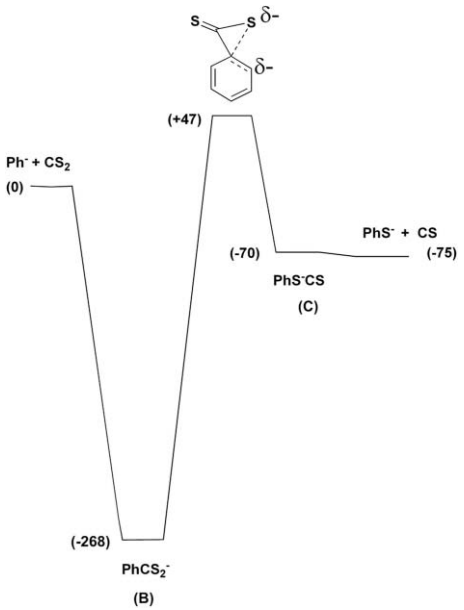


Fig. 1 The *ipso* rearrangement of $PhCS_2^-$. Energies at the UCCSD(T)/6-31+G(d,p)//B3LYP/6-31+G(d,p)] level of theory. Relative free energies (ΔG) in kJ mol^{-1}. Full details of geometries and energies of minima and transition states are recorded in Supplementary table 1.†

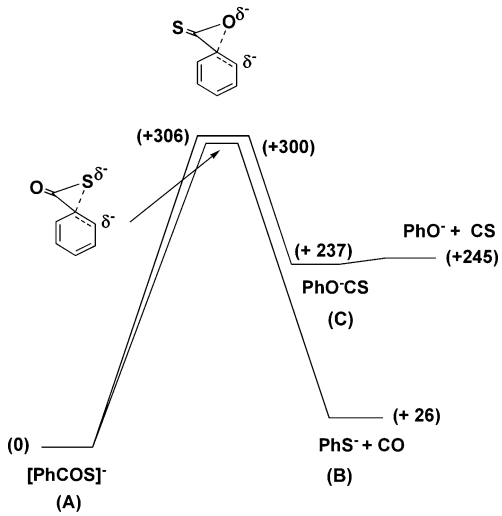


Fig. 2 The *ipso* rearrangements of $[PhCOS]^-$. Energies at the UCCSD(T)/6-31+G(d,p)//B3LYP/6-31+G(d,p)] level of theory. Relative free energies in kJ mol^{-1}. Full details of geometries and energies of minima and transition states are recorded in Supplementary table 2.†

The theoretical results are consistent with experiments, where the relative abundance of the peak due to $C_6H_5S^-$ is greater than that of $C_6H_5O^-$.

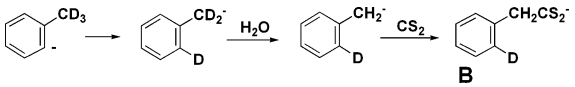
2. Reactions of the benzyl and *ortho*-tolyl anions with CS_2

The reactions of these two anions with CS_2 give adducts whose characteristic fragmentations differentiate between the structures of the original reacting carbanions. The precursors of the two anions were produced following electrospray ionization of phenylacetic acid and *ortho*-toluic acid to yield the two carboxylate anions which were decarboxylated following collisional activation

to yield the benzyl and *ortho*-tolyl anions respectively. The reaction of these two anions with CS_2 gave adducts whose fragmentations were probed using the CID MS4 scanning procedure. Decomposition of $PhCH_2CS_2^-$ gave only one fragmentation, yielding a pronounced peak corresponding to the $[PhCH_2CS_2^- - H_2S]^-$ ion (*m*/*z* 133). When this procedure was repeated with the D labelled species $PhCD_2^-$, the adduct $PhCD_2CS_2^-$ lost only D_2S. This process is shown in eqn (3): decomposition of $PhCH_2CS_2^-$ gives $PhCCS^-$ and H_2S, an endothermic process (+120 kJ mol^{-1}) at the UCCSD(T)/6-31+G(d,p)//B3LYP/6-31+G(d,p) level of theory (see Supplementary Table 3†).

$$PhCH_2CS_2^- \rightarrow Ph{\cdot}CH(=S)SH \rightarrow [(PhCH{=}C{=}S)^-SH] \rightarrow PhC{\equiv}CS^- + H_2S \quad (3)$$

The situation with the *ortho*-tolyl anion is more complex: the adduct formed with CS_2 when collisionally activated shows competitive losses of H_2S and CS. The loss of CS is simply the *ipso* rearrangement (*cf.* Fig. 1) of the expected adduct *ortho*-$CH_3C_6H_4CS_2^-$. But how is H_2S lost? This was uncovered when the reaction between the D labelled *ortho*-$CD_3C_6H_4^-$ and CS_2 was studied. The decarboxylation process formed *ortho*-$CD_3C_6H_4^-$ and if this anion was allowed to react immediately with CS_2, the adduct lost only CS by a standard *ipso* rearrangement. If, in contrast, the *ortho*-$CD_3C_6H_4^-$ anion was allowed to remain in the trap for 10 microseconds, it back exchanged two D for H (reaction with residual H_2O from the electrospray ionization process). This ion formed an adduct with CS_2 which, on collisional activation, lost H_2S exclusively. This can only be due to the process shown in eqn (4): namely D transfer to the *ortho* position followed by D/H exchange of the two remaining benzylic deuteriums by water (a process of the type first reported by DePuy *et al* [27,28]) to yield the D_1 adduct **B** which then loses H_2S (see eqn (4) and *cf.* eqn (3)). The interconversion of the *ortho*-tolyl and benzyl anions is an exothermic process (–53 kJ mol^{-1}) with a barrier of 179 kJ mol^{-1} at the UCCSD(T)/6-31+G(d,p)//B3LYP/6-31+G(d,p) level of theory (see Fig. 3 and Supplementary table 4†).



(4)

3. The reactions of the β-phenylethyl anion and other isomers with CS_2

The question as to whether the β-phenylethyl anion ($PhCH_2CH_2^-$) is stable has been a matter of debate for almost 20 years. Nibbering *et al.*[30] presented data which showed that the β-phenylethyl anion rearranges to the cyclised *ipso* form on collisional activation in a conventional mass spectrometer, while Squires and Graul[31] proposed that the β-phenylethyl anion was stable in a flowing afterglow instrument, because the ion formed by decarboxylation of $PhCH_2CH_2CO_2^-$ was thermalised by the helium carrier gas, and had a gas phase basicity (ΔG°_{acid}) of 1699 ± 13 kJ mol^{-1}, a value consistent with that expected for $PhCH_2CH_2^-$.

The reaction coordinate calculations [at the UCCSD(T)/6-31+G(d,p)//B3LYP/6-31+G(d,p) level of theory] of relevant $C_8H_9^-$ isomers provide some interesting results (see Fig. 4 and Supplementary table 5†). First, $PhCH_2CH_2^-$ (**A**) can undergo a 1,2-H transfer over a transition state (+145 kJ mol^{-1}) to yield Ph^-CHCH_3 (**D**) in an exothermic reaction (–104 kJ mol^{-1}). Second,

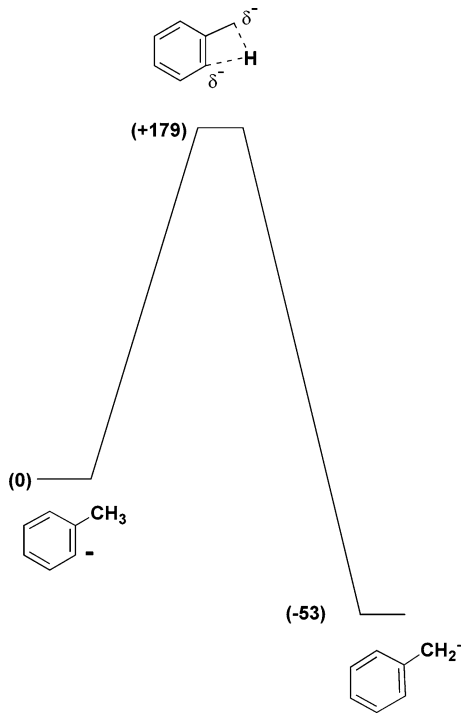


Fig. 3 The interconversion of the benzyl and *ortho*-tolyl anion. Energies at the UCCSD(T)/6-31+G(d,p)//B3LYP/6-31+G(d,p)] level of theory. Relative free energies in kJ mol^{-1}. Full details of geometries and energies of minima and transition states are recorded in Supplementary table 4.†

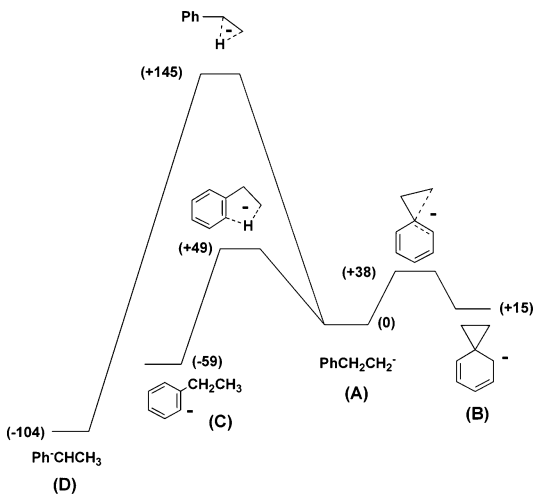


Fig. 4 The interconversions of $PhCH_2CH_2^-$ (**A**), Ph^-CHCH_3 (**D**), *ortho*-C_2H_5–$C_6H_4^-$ (**C**) and the cyclised species (**B**). Energies at the UCCSD(T)/6-31+G(d,p)//B3LYP/6-31+G(d,p)] level of theory. Relative free energies in kJ mol^{-1}. Full details of geometries and energies of minima and transition states are recorded in Supplementary table 5.†

$PhCH_2CH_2^-$ can H^+ transfer from the *ortho* position to give *ortho*-$C_2H_5C_6H_4^-$ (**C**) [barrier (+49 kJ mol^{-1}), reaction exothermic (–59 kJ mol^{-1})]. However, the electron affinity of $PhCH_2CH_2^{\bullet}$ at the G3B3 level of theory is calculated to be 0.215 eV (21 kJ mol^{-1}), so these two H transfer processes are unfavourable compared with electron loss from $PhCH_2CH_2^-$. Finally, the data shown in Fig. 4 indicates that the conversion of $PhCH_2CH_2^-$ (**A**) to the cyclic isomer (**B**) is endothermic (+15 kJ mol^{-1}) and has a modest barrier

to the transition state of 38 kJ mol^{-1}. This interconversion and electron loss from $PhCH_2CH_2^-$ should therefore be competitive. These theoretical data are consistent with previous studies, namely (i) Nibbering *et al.* finding rearrangement of $PhCH_2CH_2^-$ on collisional excitation,[30] and (ii) Squires and Graul suggesting that $PhCH_2CH_2^-$ is stable when the ion is efficiently thermalized by the helium carrier gas in the flowing afterglow drift tube.[31]

The collision induced mass spectrum of the adduct formed between "$PhCH_2CH_2^-$" (by decarboxylation of $PhCH_2CH_2CO_2^-$) and CS_2 shows pronounced loss of H_2S. The analogous spectra of $Ph(CH_3)CHCS_2^-$ and *ortho*-C_2H_5–C_6H_4-CS_2^- do not exhibit loss of H_2S. *Ortho*-$C_2H_5C_6H_4$-CS_2^- eliminates CS by the standard *ipso* rearrangement (data not shown but *cf.* Fig. 1)], while $Ph(CH_3)CHCS_2^-$ yields $Ph(CH_3)CH^-$ at low CS_2 pressures. It can therefore be concluded that $PhCH_2CH_2^-$ neither isomerizes to Ph^-CHCH_3 nor to *ortho*-$C_2H_5C_6H_4^-$ prior to or during reaction with CS_2 in the LCQ mass spectrometer.

The two D labelled species $PhCH_2CD_2CS_2^-$ and $PhCD_2CH_2CS_2^-$ were formed in the Waters QTOF2 mass spectrometer [by deprotonation under electrospray ionization of $PhCH_2CD_2CS_2H$ and $PhCD_2CH_2CS_2H$ in methanol]. These two dithiocarboxylate anions are those which would be formed by the ion molecule reactions between the appropriately D-labelled β-phenylethyl anion and CS_2 in the LCQ spectrometer. CID MS/MS of $PhCH_2CD_2CS_2^-$ shows loss of D_2S (see Fig. 5), while $PhCD_2CH_2CS_2^-$ loses H_2S. Loss of H_2S from $PhCH_2CH_2CS_2^-$ has been shown by *ab initio* calculations to occur as shown in Fig. 6 (also Supplementary table 6†).

The two D labelled species "$PhCD_2CH_2^-$" and "$PhCH_2CD_2^-$" were prepared by decarboxylation of their respective carboxylate anions in the LCQ mass spectrometer. If these anions interconvert

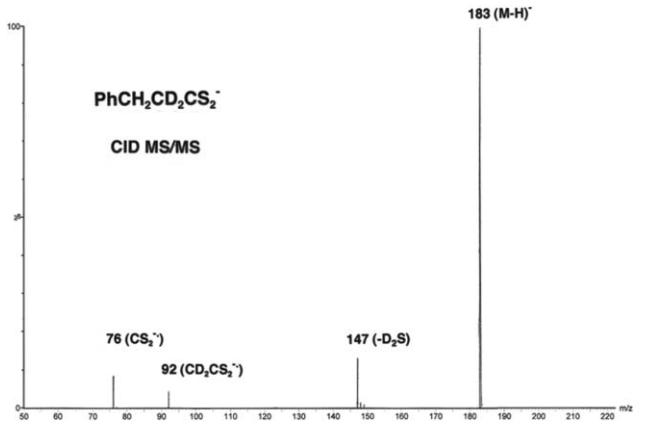


Fig. 5 The CID MS/MS of $PhCH_2CD_2CS_2^-$ using electrospray ionization with a Waters QTOF2 mass spectrometer. The collisional activation process in the QTOF2 produces more energized anions than those formed in the LCQ. Thus the peaks observed at *m/z* 92 and 76 in Fig. 5 are not observed in Fig. 7. Since H_2S is lost exclusively from $PhCD_2CH_2CS_2^-$, the small peaks at *m/z* 148 and 149 (losses of HDS and H_2S respectively) shown in this Figure are produced by undefined reactions favoured by the operation of a primary deuterium isotope effect occurring for the loss of D_2S from $PhCH_2CD_2CS_2^-$.

through the D_2 analogue of cyclic (**B**) (Fig. 4) prior to or during reaction with CS_2, the subsequent losses of H_2S : D_2S should be the same from both labelled adducts (assuming no deuterium isotope effect is operating). If there is no cyclization then specific losses of H_2S and D_2S should be observed, as seen in the QTOF2 spectra described above. The LCQ data are as follows. The adduct formed from "$PhCD_2CH_2^-$" and CS_2 loses H_2S, while that from

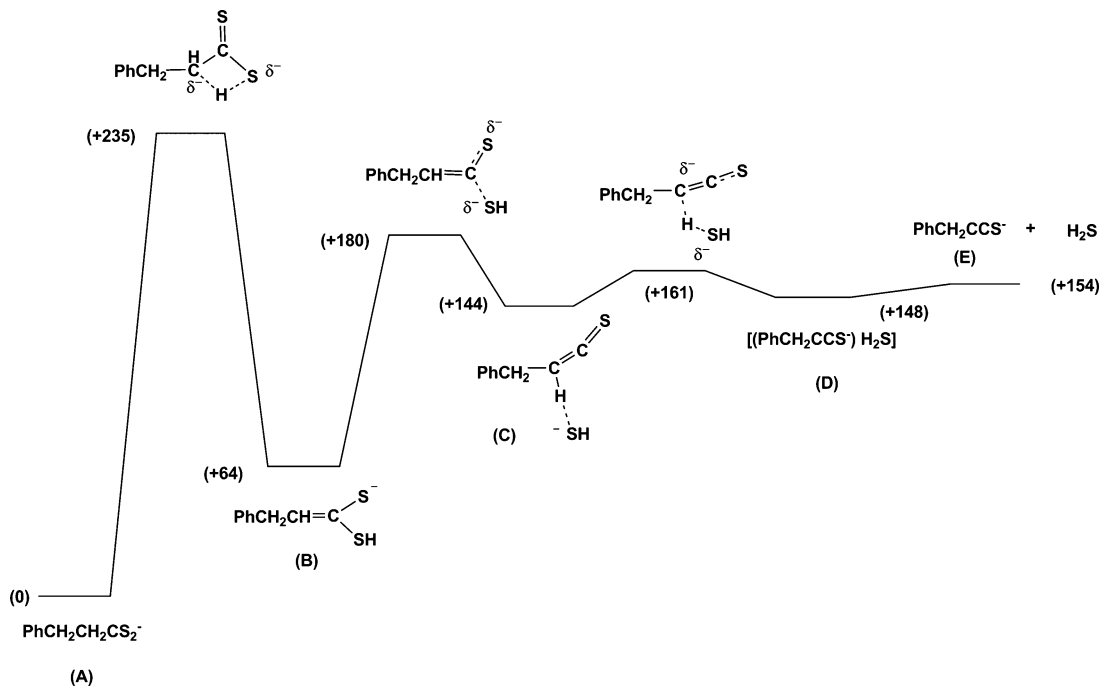


Fig. 6 Reaction coordinate profile for the dissociation of $PhCH_2CH_2CS_2^-$ to $PhCH_2CCS^-$ + H_2S. Energies at the UCCSD(T)/6-31+G(d,p)//B3LYP/6-31+G(d,p)] level of theory. Relative free energies in kJ mol^{-1}. Full details of geometries and energies of minima and transition states are recorded in Supplementary table 6.† The reaction $PhCH_2CH_2^-$ + CS_2 → $PhCH_2CH_2CS_2^-$ is exothermic by 330 kJ mol^{-1}.

"$PhCH_2CD_2^-$" and CS_2 loses D_2S (see Fig. 7). The spectrum shown in Fig. 7 does not change when the trapping time of the reactant ion is increased to 10 μsec.

$$PhCH_2CH_2CO_2^- \rightarrow PhCH_2CH_2^- + CO_2 \quad (5)$$

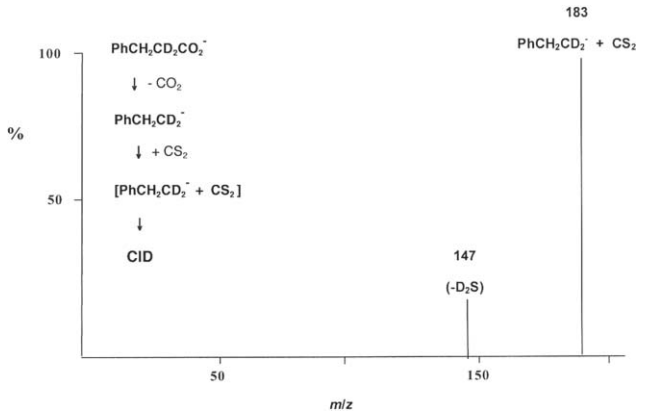


Fig. 7 The CID MS/MS/MS/MS scan of "$PhCH_2CD_2CS_2^-$" formed by the reaction of CS_2 with "$PhCH_2CD_2^-$" (formed from $PhCH_2CD_2CO_2^-$). Electrospray ionization of $PhCH_2CD_2CO_2H$ using a modified[36] Finnigan LCQ mass spectrometer.

The decarboxylation reaction shown in eqn (5) is calculated to be endothermic (+231 kJ mol^{-1}) at the UCCSD(T)/6-31+G(d,p)//B3LYP/6-31+G(d,p) level of theory (see Supplementary table 7†). Thus $PhCH_2CH_2CO_2^-$ on collisional activation must produce a precursor with sufficient energy (231 kJ mol^{-1}) in order to effect decarboxylation. Collisional processes will produce energized precursor ions with a range of excess energies. The consequence of this is that some product ions $PhCH_2CH_2^-$ may have excess energy. The theoretical results shown in Fig. 4 indicate that $PhCH_2CH_2^-$ (**A**) needs only 38 kJ mol^{-1} of excess energy in order to effect conversion to *ipso* species **B**. The experiments already carried out for the reactions of $PhCH_2CD_2^-$ and $PhCD_2CH_2^-$ with CS_2 show that there is no evidence of the *ipso* anion (**B**) (see Fig. 4) reacting with CS_2 during the ion molecule reaction, or of **B** being involved in an equilibrium process with **A** preceding or accompanying the ion molecule reaction with CS_2. This indicates that only thermalised ions **A** (or more correctly, anions with less than 38 kJ mol^{-1} of excess energy) are reacting with CS_2 in the LCQ ion trap (*cf.* Gronert[34,35]).

Conclusions

1. The reaction between $C_6H_5^-$ and CS_2 in the gas phase gives an adduct $C_6H_5CS_2^-$ which, when energized, rearranges *via* an *ipso* transition state to yield $C_6H_5S^-$ and CS.

2. The respective reactions between $C_6H_5CH_2^-$ and *ortho*-$CH_3C_6H_5^-$ with CS_2 give adducts which can be readily distinguished by their collision induced dissociations; *i.e.* the adduct with $C_6H_5CH_2^-$ loses H_2S, while that with *ortho*-$CH_3C_6H_5^-$ loses both H_2S and CS_2, and

3. Decarboxylation of $C_6H_5CH_2CH_2CO_2^-$ gives $C_6H_5CH_2CH_2^-$ which reacts with CS_2 without rearrangement, to yield $C_6H_5CH_2CH_2CS_2^-$.

Experimental

Mass spectrometry

All ion molecule reactions were carried out using electrospray ionization with a Finnigan LCQ ion trap mass spectrometer, modified[36] to allow ion-molecule reactions to be carried out by the incorporation of additional inlets for introduction of an extra reagent gas or liquid (in this case CS_2). The reagent CS_2 was injected into the system by syringe at a rate of 5 mL min^{-1}. Typical electrospray conditions involved a needle potential of 4.0 to 5.0 kV and a heated capillary temperature of 180 °C. Ions undergoing ion-molecule reactions in the LCQ have been essentially shown to be at room temperature.[34,35] These experiments were investigated using the MS_n capability of the LCQ instrument. As an example, CID of $C_6H_5CO_2^-$ to $C_6H_5^-$ and CO_2 utilises an MS/MS scan, reaction of $C_6H_5^-$ with CS_2 (MS/MS/MS) and finally, decomposition of the $C_6H_5^-$ plus CS_2 adduct utilises an MS/MS/MS/MS scan.

Electrospray CID MS/MS spectra of $ArCO_2^-$, $ArCOS^-$ and $ArCS_2^-$ anions were measured using a Waters QTOF2 hybrid orthogonal acceleration time-of-flight mass spectrometer (Waters/Micromass, Manchester, UK) with a mass range to *m/z* 10,000. The QTOF2 is fitted with an electrospray (ES) source in an orthogonal configuration with a *Z*-spray interface. Samples were dissolved in acetonitrile–water (1 : 1 v/v) and infused into the ES source at a flow rate of 5 mL min^{-1}. Experimental conditions were as follows: capillary voltage 3.1 kV, source temperature 80 °C, desolvation temperature 150 °C, and cone voltage 50 V. Tandem mass spectrometry (MS/MS) data were acquired using argon as the collision gas and the collision energy was set to give maximum fragmentation.

Theoretical methods

Geometry optimizations were carried out with the B3LYP/6-31+G(d,p) basis set [energies at UCCSD(T)/6-31+G(d,p) within the GAUSSIAN 03 suite of programs.[37] Stationary points were characterized as either minima (no imaginary frequencies) or transition states (one imaginary frequency) by calculation of the frequencies using analytical gradient procedures. The minima connected by a given transition structure were confirmed by intrinsic reaction coordinate (IRC) calculations.[38] The calculated frequencies were also used to determine zero-point vibrational energies.

The G3B3 level of theory[39] was used to calculate electron affinities (the difference in energy between the appropriate anion and the corresponding radical). Three levels of theory were used for chosen standards $CH_3CO_2^{\bullet}$ and $HCO_2^{\bullet}$. The computed values obtained were compared with experimental values as shown below:-

Level of theory $CH_3CO_2^{\bullet}$ $HCO_2^{\bullet}$
Experimental 3.470 eV[40] 3.541 eV[41]
G2[42] 3.499 eV 3.715 eV
G3B3 3.319 eV 3.555 eV
UCCSD//B3LYP 3.082 eV 3.474 eV

The G3B3 level of theory was used for calculating the following electron affinities because of reasonable accuracy (see above) and efficiency of computer time usage:- $PhCS_2^{\bullet}$ 3.345 eV and $PhCH_2CH_2^{\bullet}$ 0.215 eV.

All calculations were carried out using the South Australian Partnership for Advanced Computing (SAPAC) Facility.

Materials/synthesis

The following were purchased from Sigma-Aldrich and were used without purification:- (i) argon gas, carbon disulfide, benzoic acid, thiobenzoic acid, phenylacetic acid, *ortho*-toluic acid, 1-phenylpropionic acid, 2-phenylpropionic acid, *ortho*-ethylbenzoic acid, and 1,2-dibromobenzene; (ii) CD_3I ($d_3 > 99.5\%$).

Dithiobenzoic acid was made by a standard Grignard reaction between bromobenzene and carbon disulfide[43] [$(M - H)^-$ m/z 153; m.p. dec. > 200 °C; lit[44] 208 °C).

Dithiophenyl acetic acid (benzene ethane dithioic acid) was prepared by a standard Grignard reaction using benzyl chloride and carbon disulfide.[43] (yield 57%; m.p. 17–19 °C, lit.[45] 20 °C

o-Methyl(d_3)benzoic acid [m.p. 103–104 °C (lit.[46] 104–105 °C; $d_3 = 99.5\%$) was made by a Grignard sequence using d_3-methyl iodide ($d_3 = 99.5\%$) and commencing with the diethylacetal of *o*-bromobenzaldehyde.[47]

2,2-Dideuterophenylacetic acid [m.p. 77–78 °C (lit.[48] 78 °C; $d_2 = 95\%$] was prepared by two cycles of exchange of phenylacetic acid with deuterium oxide using a standard method.[48]

2-Phenyl-2,2-dideutero-1-bromoethane. 2,2-dideuterophenylacetic acid was treated with lithium aluminium hydride in tetrahydrofuran (THF) at 0° by a standard method[49] giving 2-phenyl-2,2-dideuteroethanol (90% yield after vacuum distillation; d_2=95%], which was treated with bromine and triphenyl phosphine in dichloromethane by a standard method,[50] to give 2-phenyl-2,2-dideutero-1-bromoethane as a colourless oil after vacuum distillation (yield 65%; $d_2 = 95\%$).

2-Phenyl-1,1-dideutero-1-bromoethane. Phenylacetic acid was treated with lithium aluminium deuteride in THF at 0° by a standard method[49] giving 2-phenyl-1,1-dideuteroethanol as a colourless oil (after vacuum distillation) (yield 91%; $d_2 = 98\%$), which was treated with bromine and triphenyl phosphine in dichloromethane by a standard method[50] to give 2-phenyl-1,1-dideutero-1-bromoethane as a colourless oil (after vacuum distillation) (yield 83%; $d_2 = 98\%$).

2,2-Dideutero-3-phenylpropionic acid. 2-Phenyl-1,1-dideutero-1-bromoethane in THF was allowed to react (by a standard Grignard reaction[51]) with magnesium in THF under reflux, followed by addition of solid carbon dioxide to give 2,2-dideutero-3-phenylpropionic acid [m.p. 46–48 °C (lit.[47] 47–48 °C); yield 62%; $d_2 = 98\%$].

3,3-Dideutero-3-phenylpropionic acid. 2-Phenyl-2,2-dideutero-1-bromoethane in THF was allowed to react with magnesium in THF under reflux.[51] Addition of solid CO_2 gave 3,3-dideutero-3-phenylpropionic acid [m.p. 46–48 °C (lit.[47] 47–48 °C); yield 65%; $d_2 = 95\%$].

2,2-Dideutero-3-phenylpropane dithiolic acid. 2-Phenyl-1,1-dideutero-1-bromoethane in THF was allowed to react with Mg in THF, followed by addition of CS_2 and a catalytic amount of CuCl (in THF) at −50 °C.[43] Workup gave 2,2-dideutero-3-phenylpropanedithiolic acid as an unstable red–orange oil [$(M - H)^-$ m/z 183; 23% yield; $d_2 = 98\%$] which was used immediately in the gas phase ion chemistry experiments to form $PhCH_2CD_2CS_2^-$ in the QTOF2 mass spectrometer.

3,3-Dideutero-3-phenylpropane dithiolic acid. 2-Phenyl-2,2-dideutero-1-bromoethane in THF was allowed to react with Mg in THF, followed by addition of CS_2 and a catalytic amount of CuBr in THF at −50 °C.[43] 3,3-Dideutero-3-phenylpropanedithiolic acid was isolated as an unstable red–orange oil [$(M - H)^-$ m/z 183; 25% yield, $d_2 = 95\%$]. This was used immediately in the gas phase experiment in the QTOF2 to form $PhCD_2CH_2CS_2^-$.

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References

1 L. A. Warren and S. Smiles, *J. Chem. Soc.*, 1930, 1327; C. S. McClement and S. Smiles, *J. Chem. Soc.*, 1937, 1016; W. E. Truce, E. M. Kreider and W. W. Brand, *Org. React.*, 1970, **18**, 99; D. M. Schmidt and G. E. Bonvicino, *J. Org. Chem.*, 1984, **49**, 1664 and references cited therein.
2 D. G. Musaev, A. L. Galloway and F. M. Menger, *THEOCHEM*, 2004, **679**, 45.
3 L. H. Mitchell and N. C. Barvian, *Tetrahedron Lett.*, 2004, **45**, 5669.
4 M. Mizuno and M. Yamano, *Org. Lett.*, 2005, **7**, 3629.
5 L. El Kaim, M. Gizolme and L. Grimaud, *Org. Lett.*, 2006, **8**, 5021.
6 J. B. Xiang, L. Y. Zheng and H. X. Lie, *Tetrahedron*, 2008, **64**, 9101.
7 H. Zuo, L. Meng, M. Ghate, K.-H. Hwang, Y. K. Cho, S. Chandrasekhar, C. R. Reddy and D.-S. Shin, *Tetrahedron Lett.*, 2008, **49**, 3827.
8 J. B. Xiang, H. X. Xie and D. S. Wen, *J. Org. Chem.*, 2008, **73**, 3281.
9 J. H. Li and J. S. Wang, *Aust. J. Chem.*, 2009, **62**, 176.
10 W. B. Motherwell and A. M. K. Pannell, *J. Chem. Soc., Chem. Commun.*, 1991, 877.
11 R. Caddick, C. L. Shering and S. N. Wadman, *Tetrahedron*, 2000, **56**, 465.
12 Ryokawa and H. Togo, *Tetrahedron*, 2001, **57**, 5915.
13 M. Tada, H. Shijuna and M. Nakamura, *Org. Biomol. Chem.*, 2003, **1**, 2499.
14 E. Bacqué, M. El Qacemi and S. Z. Zard, *Org. Lett.*, 2005, **7**, 3817.
15 T. J. Snape, *Chem. Soc. Rev.*, 2008, **37**, 2452.
16 T. J. Snape, *Synlett*, 2008, 2689.
17 P. C. H. Eichinger, J. H. Bowie and R. N. Hayes, *J. Am. Chem. Soc.*, 1989, **111**, 4224.
18 D .C. Graham and J. H. Bowie, unpublished observations.
19 P. C. H. Eichinger and J. H. Bowie, *Org. Mass Spectrom.*, 1992, **27**, 995.
20 J. H. Bowie, *Aust. J. Chem.*, 1971, **24**, 989.
21 H. Y. Wang, X. Zhang, Y.-L. Guo and L. Lu, *J. Am. Soc. Mass Spectrom.*, 2005, **16**, 1561.
22 F. Wang, *Rapid Commun. Mass Spectrom.*, 2006, **20**, 1820.
23 Y. P. Zhou, Y. J. Pan and X. T. Cao, *J. Am. Soc. Mass Spectrom.*, 2007, **18**, 1813.
24 M. Shafi, M. Hussain and S. G. Peeran, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2007, **182**, 2087.
25 M. J. Sun, W. Daim and D. Q. Liu, *J. Mass Spectrom.*, 2008, **43**, 383.
26 P. H. Lambert, S. Berlin, J. M. Lacoste, J. P. Volland, A. Krick, E. Furet, A. Botrel and P. Guenot, *J. Mass Spectrom.*, 1998, **33**, 242.
27 C. H. DePuy and V. M. Bierbaum, *Acc. Chem. Res.*, 1981, **14**, 146; and references cited therein.
28 C. H. DePuy, V. M. Bierbaum and J. J. Grabowski, *Science*, 1982, **218**, 955.

29 M. J. Raftery and J. H. Bowie, *J. Chem. Soc., Perkin Trans. 2*, 1988, 563.
30 W. P. M. Maas, P. A. van Veelen and N. M. M. Nibbering, *Org. Mass Spectrom.*, 1989, **24**, 546.
31 S. T. Graul and R. R. Squires, *J. Am. Chem. Soc.*, 1990, **112**, 2506, and references cited therein.
32 S. T. Graul and R. R. Squires, *Mass Spectrom. Rev.*, 1988, **7**, 263 and references cited therein.
33 J. C. Sheldon, J. H. Bowie, C. H. DePuy and R. Damrauer, *J. Am. Chem. Soc.*, 1986, **108**, 6794.
34 S. Gronert, *J. Am. Soc. Mass Spectrom.*, 1998, **9**, 845.
35 S. Gronert, L.M. Pratt and S. Mogall, *J. Am. Chem. Soc.*, 2001, **123**, 3081.
36 T. Waters, R. A. J. O'Hair and A. G. Wedd, *J. Am. Chem. Soc.*, 2003, **125**, 3384.
37 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Topyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Makajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Know, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austlin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Cliffors, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Latham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03*, Revision E; Gaussian, Inc., Wallingford, CT, 2004.
38 K. Fukui, *Acc. Chem. Res.*, 1981, **14**, 363.
39 A. G. Baboul, L. A. Curtiss, P. C. Redfern and K. Raghavachari, *J. Chem. Phys.*, 1999, **110**, 7650; L. A. Curtiss, K. Raghavachari, P. C. Redfern and J. A. Pople, *J. Chem. Phys.*, 2000, **112**, 7373.
40 Z. Lu and R. E. Continetti, *J. Phys. Chem. A*, 2004, **108**, 9962.
41 G. Caldwell, R. Renneboog and P. Kebarle, *Can. J. Chem.*, 1989, **67**, 611.
42 L. A. Curtiss, K. Raghavachari, G. W. Trucks and J. A. Pople, *J. Chem. Phys.*, 1991, **94**, 7221.
43 P. Vermeer, *Synthesis*, 1979, 432.
44 *NL patent* 1967, 6510637.
45 D. F. Aycock, *J. Org. Chem.*, 1979, **44**, 569.
46 P. A. S. Smith, *J. Am. Chem. Soc.*, 1954, **76**, 431.
47 C. C. Lee, *Tetrahedron*, 1959, **7**, 206.
48 K. Auwers, *Justus Liebigs Ann. Chem.*, 1910, **373**, 239.
49 J. Blum, S. Kraus and Y. Pickholtz, *J. Organomet. Chem.*, 1971, **33**, 227.
50 M. Orfanopoulos, I. Smonou and C. S. Foote, *J. Am. Chem. Soc.*, 1990, **112**, 3607.
51 A. I. Vogel, *A textbook of practical organic chemistry*, Third Edition pp 247-260, Longmans, Green and Co, London, 1956.