Isomerisation Reactions of β-Ethyl Anions in the Gas Phase

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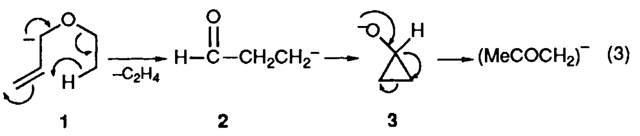
Evidence based primarily on the technique of collisional activation mass spectrometry is presented which suggests that substituted β-ethyl anions ($XCH_2CH_2^-$) are at best transient species in the gas phase often rearranging to more stable isomers, *e.g.*. $MeCOCH_2CH_2^- \longrightarrow MeCO\bar{C}HMe$, $PhCOCH_2CH_2^- \longrightarrow PhCO\bar{C}HMe$, $HOCOCH_2CH_2^- \longrightarrow MeCH_2CO_2^-$ and $CH_2{=}CHCH_2CH_2 \longrightarrow {}^-CH_2{-}CH{=}CH{-}Me$. The β-methoxycarbonylethyl anion $MeOCOCH_2CH_2^-$ is presumably unstable with respect to its radical since no peak corresponding to either this species or a stable isomer is observed.

The stabilizing influence of a substituent β to a carbanion centre has invoked considerable theoretical interest.[1–6] Both electronegative and electropositive groups are capable of stabilizing β-substituted ethyl anions $XCH_2CH_2^-$; the stabilizing energy can be determined by calculating the energy change for the reaction shown in eqn. (1).[3] There has been some debate in rationalising this stabilization in practical terms.[1,4,5] It could be due to negative (or anionic) hyperconjugation[7,8] [see formula (2)] and/or to inductive effects. It has been concluded that both of these effects are important, and that the contribution from hyperconjugative stabilization may approach 40 kJ mol^{-1} in favourable cases.[5]

$$XCH_2CH_2^- + CH_3CH_3 \longrightarrow XCH_2CH_3 + CH_3CH_2^- \quad (1)$$

$$\overset{X}{}CH_2{-}CH_2^- \longleftrightarrow \overset{X^-}{CH_2{=}CH_2} \quad (2)$$



1 **2** **3** (3)

We entered this area almost serendipitously. Firstly, we reported that loss of formaldehyde from deprotonated γ-phenylpropanol gave $PhCH_2CH_2^-$ as the first formed (but probably rearranging) species,[9] an observation confirmed by Nibbering in a cognate system.[10] Second, we showed that an unusual elimination reaction of deprotonated ether **1** yielded the acetone enolate ion, a reaction which proceeds through the intermediacy of the β-formylethyl anion **2** [eqn. (3)][11] (*cf.*[12,13]).*

The above observations led us to undertake a more extensive survey of $XCH_2CH_2^-$ species (X = MeCO, PhCO, HOCO, MeOCO and CH=CH$_2$), with respect to their formation, stability and possible isomerization. While this work was in progress a flowing afterglow study of several of these ions was reported by Squires.[14] These results will be included in the discussion below.

Results and Discussion

The following study describes attempts to detect directly a number of β-substituted ethyl anions in the gas phase. Three experimental approaches were used in an attempt to generate $XCH_2CH_2^-$ species: these are summarized in eqns. (4)–(6). The

$$XCH_2CH_2CH_2O^- \xrightarrow{CID} XCH_2CH_2^- + CH_2O \quad (4)$$

$$XCH_2CH_2CO_2^- \xrightarrow{CID} XCH_2CH_2^- + CO_2 \quad (5)$$

$$Me_3SiCH_2CH_2X + MeO^- \longrightarrow XCH_2CH_2^- + Me_3SiOMe \quad (6)$$

first involves collision-induced loss of formaldehyde from an alkoxide [eqn. (4)],[9] the second decarboxylation of an appropriate carboxylate anion,[15] and the third, the standard S_N2 (Si) displacement reaction.[11,16]

It is likely that all of these reactions may form the product anion with excess energy in a conventional chemical ionization source, consequently there is a possibility that the first formed product may either rearrange to a more stable structure or alternatively eject an electron (if the electron affinity of the corresponding radical is small). In this study we probe the structure of ions by collisional activation mass spectrometry, and by their charge reversal (positive ion) mass spectra.[17] Eqn. (6) is carried out in the source of our ZAB 2HF instrument, and the corresponding CA and CR MS/MS data were obtained with that instrument. However, a three sector instrument is required for the measurement of the spectra of the product ions of eqns. (4) and (5); the appropriate CA and CR MS/MS/MS data were determined with the MS 50 TA instrument at the University of Nebraska, Lincoln. The collisional processes (outlined above) increase the energy of the decomposing ion, so that even if some initially formed $XCH_2CH_2^-$ species survive intact in the ion source, rearrangement following collisional activation in the collision cell seems likely.

Graul and Squires[14] have used the decarboxylation reaction (5) to form certain $XCH_2CH_2^-$ species in a flowing afterglow instrument. Using this facility it is possible to both thermalise ions (by collisions with the flow gas) and to control the collision energy required for dissociation. Thus there is some probability of directly observing β-ethyl anions in a flowing afterglow system.

The β-Acetylethyl Anion.—A stable ion *m/z* 71 is formed by all three processes shown in eqns. (4)–(6) when X = MeCO. In principle, the laevulinate ion **4** could undergo the required decarboxylation process [eqn. (7)] or lose acetaldehyde [eqn. (8)], to form ions *m/z* 71. This matter was resolved by the

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* In order to substantiate the intermediacy of **2** and **3** [eqn. (3)], the two intermediates were synthesized by unambiguous routes. Both rearranged under the reaction conditions to $(MeCOCH_2)^-$.[11]

Table 1 Collisional activation and charge reversal mass spectra of $C_4H_7O^-$ (*m*/*z* 71) ions

Precursor (*m*/*z*)	Daughter ion (*m*/*z*)	Spectrum type	Spectrum [*m*/*z* (abundance)]
$MeCO(CH_2)_2CO_2^-$ (115)	'$MeCOCH_2CH_2^-$' (71)	CA MS/MS/MS	See Fig. 1
		CR MS/MS/MS[a]	57 (4), 56 (10), 55 (13), 54 (13), 53 (13), 43 (62), 42 (100), 41 (35), 39 (28), 29 (40), 28 (30), 27 (72), 26 (37), 15 (17), 14 (9), 13 (2)
$(MeCOEt{-}H)^-$ (71)		CA MS/MS[a]	70 (100), 69 (59), 56 (5), 55 (12), 53 (5), 43 (5), 41 (20)
		CR MS/MS[a]	57 (5), 56 (7), 55 (10), 54 (4), 53 (7), 43 (68), 42 (100), 41 (31), 39 (28), 29 (30), 28 (21), 27 (45), 15 (8), 14 (2)

[a] There are always abundance differences (particularly for $-H^{\bullet}$, $-H_2$ and the low mass regions) when comparing the MS/MS/MS (MS 50 TA) and MS/MS (VG ZAB 2HF) data, since the spectra are measured under different conditions (particularly the collision cell pressures—see Experimental section). Nevertheless, the spectra are visually very similar.

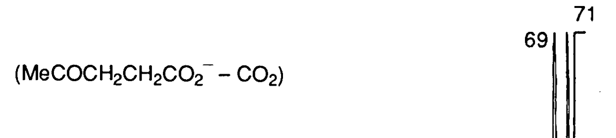
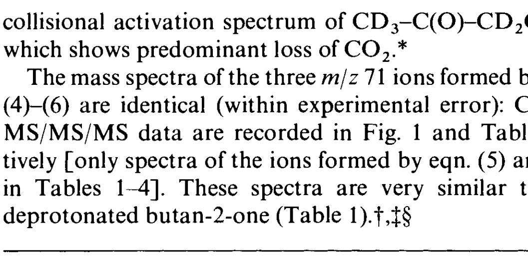


Fig. 1 CA mass spectrum (MS/MS/MS) of the $C_4H_7O^-$ ion formed by decarboxylation of the laevulinate anion. MS 50 TA instrument

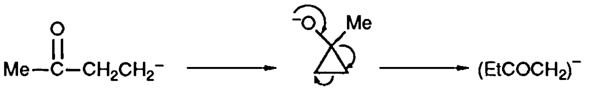


$$\underset{\mathbf{4}}{MeC(O)CH_2CH_2CO_2^-} \longrightarrow MeC(O)CH_2CH_2^- + CO_2 \quad (7)$$

$$MeC(O)CH_2\bar{C}HCO_2H \longrightarrow [MeCO^-(CH_2{=}CHCO_2H)] \longrightarrow CH_2{=}CHCO_2^- + MeCHO \quad (8)$$

collisional activation spectrum of $CD_3{-}C(O){-}CD_2CH_2CO_2^-$, which shows predominant loss of CO_2.*

The mass spectra of the three *m*/*z* 71 ions formed by reactions (4)–(6) are identical (within experimental error): CA and CR MS/MS/MS data are recorded in Fig. 1 and Table 1 respectively [only spectra of the ions formed by eqn. (5) are recorded in Tables 1–4]. These spectra are very similar to those of deprotonated butan-2-one (Table 1).†,‡§



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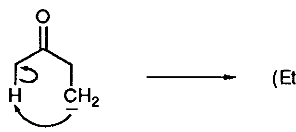
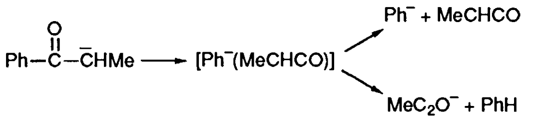


(10)

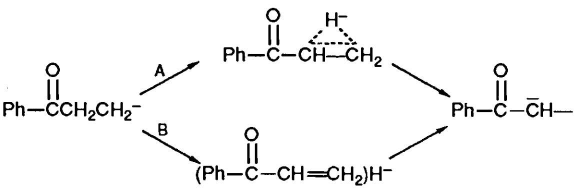
There are several possibilities for the rearrangement of the β-acetylethyl anion. The first [eqn. (9)] is directly analogous to the rearrangement of the β-formylethyl anion, [eqn. (3)], while the second, [eqn. (10)], is a simple proton transfer reaction. These processes may be differentiated by consideration of the spectra (Table 1) of the ion formed by loss of CO_2 from $CD_3COCD_2CH_2CO_2^-$. Reaction (9) will lead to a mixture of $CD_3CH_2COCD_2^-$ and $CD_3CD_2COCH_2^-$: these ions should form DC_2O^- and HC_2O^- in the ratio 1:1 (in the absence of an isotope effect) (*cf.* Fig. 1). Reaction (10) will form $CH_2DCD_2COCD_2^-$ which should decompose to form DC_2O^- exclusively. Experimentally, the ratio of DC_2O^- to HC_2O^- is 9:1, thus proton transfer [eqn. (10)] is the predominant pathway.

The β-Benzoylethyl Anion.—When X = PhCO, the reactions (4)–(6) all yield the same product *m*/*z* 133, identified as deprotonated phenyl ethyl ketone by the data shown in Table 2. The characteristic fragmentations of this ion are shown in eqns. (11) and (12) [see Fig. 2(*a*)].

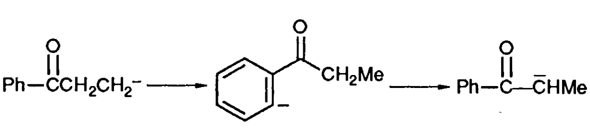


$$PhC(O)\bar{C}HMe \longrightarrow [Ph^-(MeCHCO)] \longrightarrow Ph^- + MeCHCO \quad (11)$$

$$[Ph^-(MeCHCO)] \longrightarrow MeC_2O^- + PhH \quad (12)$$



(13)



(14)

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* The spectrum of $CD_3COCD_2CH_2CO_2^-$ is as follows [*m*/*z* (loss) abundance]: 119, 118 ($H^{\bullet}$,$D^{\bullet}$ unresolved) 25, 101(HOD) 12, 100 (D_2O) 38, 76 (CO_2) 100 and 73 (CD_3CHO) 8.

† Deprotonation of butan-2-one gives two enolate ions which equilibrate under conditions of collisional activation.[18]

‡ Graul and Squires[14] propose that some $MeCOCH_2CH_2^-$ remains unrearranged in flowing afterglow experiments. They believe that the presence of *m*/*z* 43 (*i.e.* $MeCOCH_2CH_2^- \longrightarrow MeCO^- + C_2H_4$) indicates the presence of $MeCOCH_2CH_2^-$. That may well be correct, but *m*/*z* 43 is also a product ion in the spectrum of deprotonated butan-2-one [see Fig. 1 (*i.e.* $^-CH_2COCH_2Me \longrightarrow MeCOCH_2CH_2^- \longrightarrow MeCO^- + C_2H_4$)].

§ The presence of the small peak at *m*/*z* 27 $(C_2H_3)^-$ in Fig. 1 could point to a minor amount of unrearranged $MeCOCH_2CH_2^-$ [*i.e.* $MeCOCH_2CH_2^- \longrightarrow [(C_2H_4)MeCO^-] \longrightarrow C_2H_3^- + MeCHO$ since this ion is not observed in the spectrum of the deprotonated butan-2-one

Table 2 Collisional activation and charge reversal mass spectra of $C_9H_9O^-$ ions

Precursor (m/z)	Daughter ion (m/z)	Spectrum type	Spectrum [m/z (abundance)]
$PhCO(CH_2)_2CO_2^-$ (177)	'$PhCOCH_2CH_2^-$' (133)	CA MS/MS/MS^a CR MS/MS/MS^a	132 (100), 131 (40), 115 (1), 103 (3), 77 (20), 55 (9) 131 (4), 115 (14), 105 (62), 102 (17), 89 (14), 77 (100), 63 (12), 55 (5), 50 (30), 39 (6)
$C_6D_5CO(CH_2)_2CO_2^-$ (182)	'$C_6D_5COCH_2CH_2^-$' (138)	CA MS/MS/MS	137/136 (unresolved, 100), 135 (30), 119 (1), 118 (1), 107 (1), 106 (1), 82 (31), 81 (31), 55 (22)
$PhCO\bar{C}HMe$ (133)		CA MS/MS^a CR MS/MS^a	See Fig. 2(*a*) 131 (2), 115 (10), 105 (43), 102 (11), 89 (16), 77 (100), 63 (15), 55 (9), 50 (34), 39 (7)
$(PhCH_2COMe\text{-}H)^-$ (133)		CA MS/MS	See Fig. 2(*b*)

^{a} See footnote *a* Table 1.

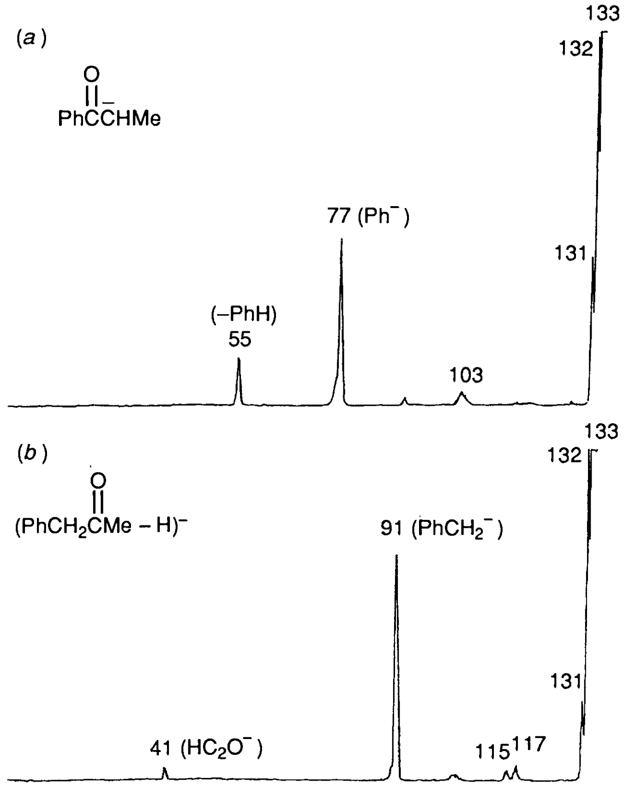
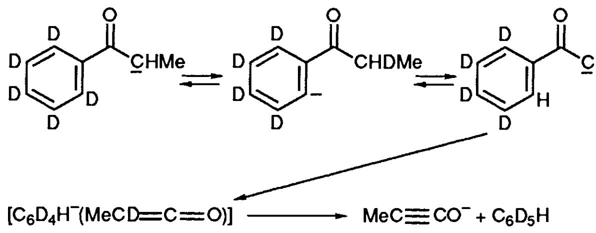


Fig. 2 (*a*) CA mass spectrum (MS/MS) of deprotonated ethyl phenyl ketone. VG ZAB 2HF instrument; (*b*) CA mass spectrum (MS/MS) of deprotonated 1-phenylpropan-2-one. VG ZAB 2HF instrument

The mechanism of this isomerization is particularly interesting. A phenyl anion migration mechanism [*cf.* eqns. (3) and (9)] does not occur, since the product of such a reaction would be $(PhCH_2COCH_2)^-$ [see Fig. 2(*b*) and *cf.* Table 2]). A facile proton transfer occurs for the β-acetyl ethyl anion, but that pathway is not available in the present instance. Three possibilities need to be considered, *viz.* (i) a concerted 1,2 H^- transfer [route A, eqn. (13)]; (ii) a stepwise H^- transfer involving a Michael type mechanism [route B, eqn. (13)]; or (iii) a double proton transfer [eqn. (14)].

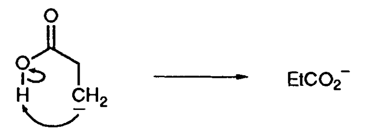
Deuterium labelling should differentiate between hydride and proton transfer. Ion m/z 138 formed by loss of CO_2 from $C_6D_5COCH_2CH_2CO_2^-$ should lose MeCHCO [eqn. (11)] and C_6D_5H [eqn. (12)] if the mechanism involves H^- transfer [eqn. (13)]. If proton transfer [eqn. (14)] operates, CH_2DCHCO and $C_6D_4H_2$ should be lost. The CA MS/MS/MS data for this ion are recorded in Table 2 and appear, at first sight, to fit neither scenario, since MeCHO, CH_2DCHCO and C_6D_5H are lost. These data cannot be accommodated by the double proton transfer ($C_6D_2H_2$ must be lost). However, the observations are consistent with a hydride transfer mechanism, *provided* the product enolate ion undergoes *ortho* H/enolate H equilibration prior to decomposition [see eqn. (15) and *cf.*[19]].



(15)

Thus we suggest that the rearrangement occurs by one of the H^- transfer mechanisms shown in eqn. (13). We prefer the stepwise route B, since concerted route A will certainly be a high energy process,[20] and in principle, be symmetry forbidden.[21]

The β-Hydroxycarbonyl- and β-Methoxycarbonyl Ethyl Anions.—When X = HOCO, reactions (5) and (6) yield an ion m/z 73, whose spectra (Table 3) are those of the propionate anion. The β-hydroxycarbonyl ethyl anion clearly isomerizes by the facile proton transfer mechanism shown in eqn. (16). The β-methoxycarbonyl analogue cannot isomerise in this way; how then does it react? This species (X = MeOCO) should be formed by each of the reactions (4)–(6). However, in no case was any species corresponding to m/z 87 observed.* There seems to be no reason why $MeOCOCH_2CH_2^-$ should not be formed by the standard reactions: presumably rearrangement (*e.g.* to $MeOCO\bar{C}HMe$) is unfavourable compared with electron loss.



(16)

The β-Vinyl Ethyl Anion.—Graul and Squires[14] have suggested that loss of CO_2 from the pent-4-enoate ion forms deprotonated but-2-ene in flowing afterglow experiments. This observation is based on appearance potential data. The following experiments support this conclusion.

When X is CH_2=CH, reactions (4)–(6) all yield a major ion at m/z 55. If this ion corresponds to the β-vinylethyl anion, it

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* As an example, the CA mass spectrum of $MeOCOCH_2CH_2CO_2^-$ (m/z 131) is as follows [m/z (loss) relative abundance]: 130 (H$^•$) 5, 99 (MeOH) 100, 71 (MeOCHO) 5 and 31 ($C_4H_4O_3$) 2.

Table 3 Collisional activation and charge reversal mass spectra of $C_3H_5O_2^-$ ions

Precursor (m/z)	Daughter ion (m/z)	Spectrum type	Spectrum [m/z (abundance)]
$HO_2C(CH_2)_2CO_2^-$	'$HO_2CCH_2CH_2^-$'	CA MS/MS/MS[a]	72 (11), 71 (100), 58 (3), 55 (35), 44 (39)
(117)	(73)	CR MS/MS/MS[a]	56 (2), 55 (3). 52 (2), 45 (23), 44 (76), 41 (19), 29 (49), 28 (70), 27 (100), 26 (64), 15 (7), 14 (9), 13 (3)
$EtCO_2^-$		CA MS/MS[a]	72 (33), 71 (100), 58 (5), 55 (51), 44 (33)
(73)		CR MS/MS[a]	56 (6), 55 (8), 52 (4), 45 (45), 44 (59), 41 (14), 29 (64), 28 (74), 27 (100), 26 (68), 15 (6), 14 (9), 13 (5)

[a] See footnote *a* (Table 1).

Table 4 Collisional activation and charge reversal mass spectra of $C_4H_7^-$ ions

Precursor (m/z)	Daughter ion (m/z)	Spectrum type	Spectrum [m/z (abundance)]
$CH_2{=}CH(CH_2)_2CO_2^-$	'$CH_2{=}CHCH_2CH_2^-$'	CA MS/MS/MS	54 (100), 53 (38)
(99)	(55)	CR MS/MS/MS[a]	55 (78), 54 (49), 53 (59), 52 (15), 51 (25), 50 (16), 41 (7), 40 (10), 39 (100), 38 (14), 37 (7), 29 (29), 28 (19), 27 (55), 26 (13), 15 (2), 14 (1)
$^-CH_2{-}CH{=}CH{-}Me$		CA MS/MS	54 (100), 53 (35)
(55)		CR MS/MS[a]	54 (55), 53 (49), 52 (16), 51 (28), 50 (26), 41 (5), 40 (11), 39 (100), 38 (35), 37 (20), 29 (30), 28 (21), 27 (59), 26 (28), 15 (2), 14 (2)
$CH_2{=}CH\bar{C}HMe$		CA MS/MS	54 (100), 53 (41)
(55)		CR MS/MS	55 (76), 54 (35), 53 (100), 52 (48), 51 (13), 40 (84), 39 (58), 38 (19), 28 (44), 27 (51), 26 (79), 25 (22), 15 (9)

[a] See footnote *a* Table 1.

should decompose by loss of C_2H_4 to form $CH_2{=}CH^-$ (m/z 27). The CA spectra of the three m/z 55 ions do not show this fragmentation. Instead, the ion eliminates only H' and H_2 (Table 3). The CA and CR spectra of the m/z 55 ions are very similar to those (Table 4) of deprotonated but-2-ene. This suggests the isomerisation shown in eqn. (17). Yet some caution

$$CH_2{=}CH{-}CH_2{-}CH_2^- \longrightarrow {}^-CH_2CH{=}CH{-}Me \quad (17)$$

needs to be exercised here. Unlike the previous cases considered, the CA spectra are very simple and not particularly diagnostic (showing only losses of H' and H_2). It is therefore possible that the identical CR spectra may reflect isomerisation of the cation (rather than the anion), particularly since we are dealing with small hydrocarbon ions (see ref. 22 for a discussion of this problem in charge reversal spectra). So we need additional evidence to confirm the proposed isomerisation reaction of the β-vinylethyl anion.

DePuy has recently predicted $\Delta H^\circ_{acid}(CH_2{=}CH{-}CH_2{-}CH_3)$ to be 1724 kJ mol^{-1} [ΔH°_{acid}(HA) is the energy required to effect the process HA $\longrightarrow$ $H^+ + A^-$].[23] Through the courtesy of Professor DePuy, we have been able to carry out ΔH°_{acid} bracketing experiments on the $C_4H_7^-$ ion (from decarboxylation of the pent-4-enoate anion) using the flowing afterglow facility at the University of Colorado, Boulder. This $C_4H_7^-$ ion does not deprotonate benzene or undergo exchange with C_6D_6 [$\Delta H^\circ_{acid}(C_6H_6)$ = 1676 kJ mol^{-1}][24] but it does undergo a slow exchange reaction with D_2O [$\Delta H^\circ_{acid}(D_2O)$ = 1644 kJ mol^{-1}].[25] This suggests that the conjugate acid of $C_4H_7^-$ has an acidity near 1644 kJ mol^{-1}. This value is not consistent with that associated with formation of $CH_2{=}CHCH_2CH_2^-$ (*viz.* 1724 kJ mol^{-1})[23] but it is appropriate for deprotonation of but-2-ene which should be close to the known value of prop-2-ene [$\Delta H^\circ_{acid}(CH_2{=}CH{-}CH_3)$ = 1635 kJ mol^{-1}].[26]

$$CH_2{=}CHCH_2CH_2^- \longrightarrow [(CH_2{=}CH{-}CH{=}CH_2)H^-] \longrightarrow \bar{C}H_2{-}CH{=}CH{-}Me \quad (18)$$

Thus the β-vinylethyl anion is unstable to isomerisation to deprotonated but-2-ene under the experimental conditions employed. A mechanistic study (involving deuterium labelling) to determine the mode of isomerisation was not undertaken in this case because of the dearth of information provided by the CA spectra of $C_4H_7^-$ ions. However, the most plausible mechanism involves the stepwise hydride ion transfer shown in eqn. (18).

Conclusions

Following our earlier work on the β-formylethyl anion,[11] we find that we are unable to directly observe $XCH_2CH_2^-$ ions (X = MeCO, PhCO, HOCO, MeOCO and $CH_2{=}CH$). Such species either (i) rearrange to stable isomers either on formation or following collisional activation (X = MeCO, PhCO, HOCO and $CH_2{=}CH$) or (ii) eject an electron to form the corresponding radical (probably for X = MeOCO).

Experimental

CA mass spectra were recorded with a Vacuum Generators ZAB 2HF mass spectrometer operating in the negative chemical-ionization mode.[27] All slits were fully open to obtain maximum sensitivity and to minimize energy-resolution effects.[28] The chemical ionization slit was used in the ion source: ionizing energy 70 eV, ion source temperature 150 °C, accelerating voltage 7 kV. The ion NH_2^- (from NH_3) was used to deprotonate all neutrals [MeO^- (from MeOH) was used in the $S_N2(Si)$ reactions (*cf.* reaction 6)]. The indicated source pressure of NH_3 (or MeOH) was 1×10^{-5} Torr.* Liquid samples were introduced through the septum inlet which was maintained at 150 °C. Solids were introduced through the direct probe—no heating was applied to the probe (the source was maintained at 150 °C). The substrate pressure was typically 5×10^{-7} Torr.

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* 1 Torr = 133.322 Pa.

The estimated total source pressure was 10^{-1} Torr. The pressure of helium in the second collision cell was 2×10^{-7} Torr, measured by an ion gauge situated between the electric sector and the second collision cell. This produced a decrease of *ca.* 10% in the main beam signal, and thus corresponds to essentially single-collision conditions.

CA and CR MS/MS/MS experiments were performed with a Kratos MS 50 TA instrument of which details have been given previously.[29] Specifically, deprotonation was effected by MeO^- (from $MeONO$[30]) in a Kratos IV chemical-ionization source: ion source temperature 100 °C, electron energy 280 eV, emission current 500 μA, accelerating voltage 8 kV. The substrate pressure was 2×10^{-5} Torr, and that of methyl nitrate 1×10^{-6} Torr. The indicated pressure of helium in each of the collision cells was 2×10^{-6} Torr producing a decrease of 30% in the main beam signal.

The flowing afterglow SIFT instrument at the University of Colorado, Boulder has been described,[31] as has the bracketing technique[32] used for the determination of gas phase acidities.

Propionic acid, laevulinic acid, phenyl ethyl ketone and 1-phenylpropan-2-one were commercial samples. The following compounds (in the order mentioned in the text) are known, and were made by reported procedures: 3-acetylpropanol,[33] 4-trimethylsilylbutan-2-one,[34] 3-benzoylpropanol,[35] 3-benzoylpropionic acid,[36] β-trimethylsilylethyl phenyl ketone,[34] β-trimethylsilylpropionic acid,[37] methyl 4-hydroxybutyrate,[38] methyl β-trimethylsilylpropanoate,[39] pent-4-enoic acid,[40] 4-trimethylsilylbut-1-ene[41] and but-1-ene.[42]

Labelled Compounds.—$[^{2}H_{3}]$-Acetyl-3,3-$[^{2}H_{2}]$-propanoic acid OD was made by exchange of laevulinic acid with D_2O ($[^{2}H_{6}] > 95\%$). (3-$[^{2}H_{5}]$-Benzoyl)propionic acid was made by acylation of $[^{2}H_{6}]$-benzene using a standard procedure[43] ($[^{2}H_{5}] = 99\%$).

Acknowledgements

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