Gas-phase Carbanion Rearrangements. Does the Wittig Rearrangement occur for Deprotonated Vinyl ethers?

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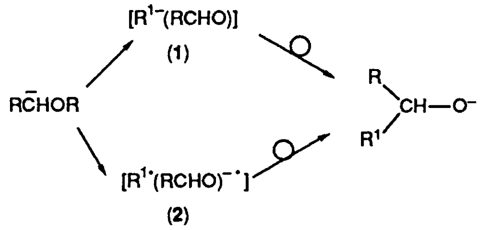
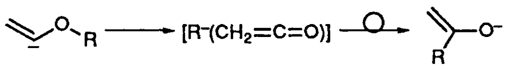
Deprotonation of alkyl vinyl ethers ($CH_2{=}CHOR$) with NH_2^- in the gas phase yields the two carbanions $CH_2{=}\bar{C}OR$ and $^-CH{=}CHOR$. The former ion can be synthesized specifically using the $S_N2(Si)$ reaction $CH_2{=}C(SiMe_3)OR + NH_2^- \rightarrow CH_2{=}\bar{C}OR + Me_3SiNH_2$: the ion undergoes several competitive and characteristic collision-induced reactions. For example, (*i*) when R ⩾ Et, elimination of an alkene, *i.e.* $CH_2{=}\bar{C}OR \rightarrow (CH_2CHO)^- + (R{-}H)$, and (*ii*) the Wittig rearrangement $CH_2{=}\bar{C}OR \xrightarrow{\ominus} CH_2{=}C(R)O^-$.

The classical Wittig rearrangement is shown in Scheme (1).[1–3] In principle, the reaction could proceed through either the ion/neutral complex (**1**) or the radical/radical anion intermediate (**2**). Experimental evidence for condensed phase reactions[4–7] can best be interpreted in terms of the radical/radical anion intermediate.[8] Wittig rearrangements are also very facile in the gas phase and have been noted for diallyl ethers[10] and benzyl alkyl ethers.[9,11,*] There have been reports of Wittig rearrangement to a vinyl carbanion centre in the condensed phase.[12] If such a reaction occurs in the gas phase, the product ion will be a ketone enolate ion (Scheme 2).



Scheme 1. R = Ph or $CH_2{=}CH^-$; R^1 = alkyl, allyl, aryl, or benzyl.



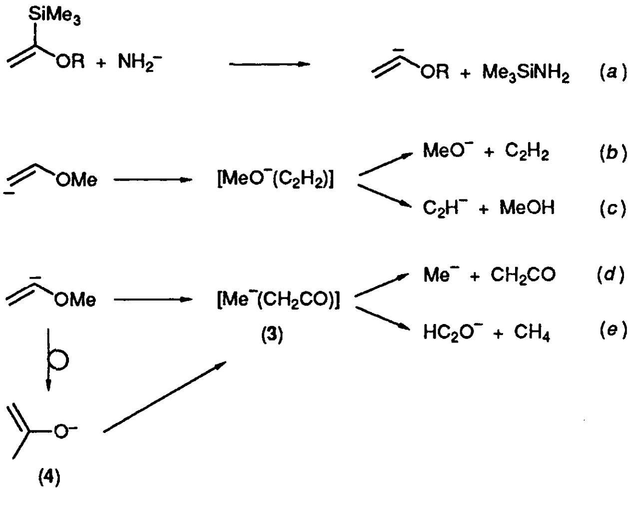
Scheme 2.

The fragmentation behaviour of ketone enolate ions has been documented;[13,14] such reactions are very characteristic and should allow ready identification of these rearrangement ions. This paper describes the collision-induced fragmentations of anions derived from alkyl vinyl ethers with a view to determining whether the ions undergo Wittig rearrangements in the gas phase.

Results and Discussion

The collisional activation mass spectra (CA MS/MS) of a variety of anions derived from alkyl vinyl ethers are listed in Table 1, together with those of the appropriate ketone enolate ions (*i.e.* the possible Wittig rearrangement products). In addition, selected spectra are illustrated in Figures 1 and 2.

It is clear from the data shown in Table 1 that the reaction of an alkyl vinyl ether with the deprotonating agent NH_2^- results in two deprotonated product ions. One product arises by deprotonation of the vinyl unit α to oxygen; the other is produced by deprotonation of the vinylic methylene group. Thus the recorded spectra of the deprotonated vinyl ethers show decompositions of both carbanions. With a view to determining specifically the spectra of α vinyl carbanions, we have prepared the appropriate anions by the $S_N2(Si)$ desilylation reaction shown in Scheme 3(*a*). The spectra of these ions are recorded in Figures 1(*b*) and 2(*b*).



Scheme 3.

The prototypical example, that of methyl vinyl ether, sets the stage for this study. The minor deprotonated species undergoes the characteristic decompositions shown in Scheme 3(*b*) and (*c*). The α carbanion, in contrast, yields Me^- [Scheme 3(*d*)] and eliminates methane to yield HC_2O^- [base peak, Scheme 3(*e*)]. The ions Me^- and HC_2O^- can be formed by two routes, *viz.* directly *via* the ion complex (**3**) or indirectly by Wittig rearrangement to the acetone enolate (**4**). The product ions HC_2O^-(m/z 41) in the spectra of both $CH_2{=}\bar{C}OMe$ and $^-(CH_2COMe)$ show within experimental error, identical widths

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[*] We will represent the intermediate in gas phase reactions (for convenience) as the ion/neutral complex (**1**). This is likely in a stepwise reaction if the electron affinity of $R^{1\cdot}$ is positive. If, in contrast, the electron affinity of $R^{1\cdot}$ is negative and that of RCHO is appreciably positive, the intermediacy of (**2**) is the more likely.

Table 1. Mass spectra of deprotonated vinyl ethers together with those of the Wittig rearrangement products.

Neutral precursor	Parent ion	Loss													
		$H^•$	$H_2,D^•$	HD	$Me^•$	CH_4	CD_3H	H_2O	C_2H_2	C_2H_4	$C_2H_2D_2$	C_2H_6	$C_2H_4D_2$	$C_2H_3D_3$	CH_2CO
$CH_2{=}CHOMe$	$(M - H^+)^-$	100				92[a]		6	2						
$CH_2{=}C(SiMe_3)OMe$	$CH_2{=}\bar{C}OMe$	100				96		8							
MeCOMe	$(MeCOCH_2)^-$	100				76[b]		4							
$CH_2{=}CHOEt$	$(M - H^+)^-$	15	6						41	100		25			
$CH_2{=}C(SiMe_3)OEt$	$CH_2{=}\bar{C}OEt$	10	5							100		16			
$CH_2{=}CHOCD_2Me$	$(M - H^+)^-$	15	20	2		14			37		100[c]		13		
$CH_2{=}CHOCH_2CD_3$	$(M - H^+)^-$	15	8	6			4		71		100[c]			66	
MeCOEt	$(M - H^+)^-$	15	100		18	51		6		10		80[d]			
$CH_2{=}CHOPr$	$(M - H^+)^-$	18	6			6		2	100	42[e]					
MeCOPr	$(M - H^+)^-$	48	36			84		1		100[g]					
$CH_2{=}CHOPr^i$	$(M - H^+)^-$	8						6	46						
$MeCOPr^i$	$(M - H^+)^-$	100	72		12	31		6		24					
$CH_2{=}CHOBu$	$(M - H^+)^-$	16				9		2	100						
$CH_2{=}C(SiMe_3)OBu$	$CH_2{=}\bar{C}OBu$	14				31									
MeCOBu	$(M - H^+)^-$	92	100			79		4		23		64			
$CH_2{=}CHOBu^t$	$(M - H^+)^-$	6				6		4	86						
$MeCOBu^t$	$(M - H^+)^-$	26	100		23	38		4							
$CH_2{=}CHOCH_2Bu^t$	$(M - H^+)^-$	80	5			12		2	100						24
$CH_2{=}C(SiMe_3)OCH_2Bu^t$	$CH_2{=}\bar{C}OCH_2Bu^t$	85	10			25			28[k]						22
$MeCOCH_2Bu^t$	$(M - H^+)^-$	100	15			66		3							
$CH_2{=}CHOPh$	$(M - H^+)^-$	100	38						77						
MeCOPh	$(M - H^+)^-$	100			1			2							

Table 1 (*continued*)

Neutral precursor	Parent ion	Loss								Formation				
		C_3H_6	C_3H_8	C_4H_8	C_4H_{10}	C_5H_{10}	C_5H_{12}	C_6H_4	C_6H_6	Ph^-	$C_2H_3^-$	C_2H^-	HO^-	Me^-
$CH_2{=}CHOMe$	$(M - H^+)^-$											6	1	5
$CH_2{=}C(SiMe_3)OMe$	$CH_2{-}\bar{C}OMe$													5
MeCOMe	$(MeCOCH_2)^-$													
$CH_2{=}CHOEt$	$(M - H^+)^-$											53		
$CH_2{=}C(SiMe_3)OEt$	$CH_2{=}\bar{C}OEt$													
$CH_2{=}CHOCD_2Me$	$(M - H^+)^-$											21		
$CH_2{=}CHOCH_2CD_3$	$(M - H^+)^-$											36		
MeCOEt	$(M - H^+)^-$										1		1	1
$CH_2{=}CHOPr$	$(M - H^+)^-$	56^f	92									14		
MeCOPr	$(M - H^+)^-$		18											
$CH_2{=}CHOPr^i$	$(M - H^+)^-$	100^h	2									4		
$MeCOPr^i$	$(M - H^+)^-$	12	81											
$CH_2{=}CHOBu$	$(M - H^+)^-$	23		41	18							6		
$CH_2{=}C(SiMe_3)OBu$	$CH_2{=}\bar{C}OBu$	39		100	30									
MeCOBu	$(M - H^+)^-$	67^i		2	18									
$CH_2{=}CHOBu^t$	$(M - H^+)^-$			100^h								1		
$MeCOBu^t$	$(M - H^+)^-$	21		3	48									
$CH_2{=}CHOCH_2Bu^t$	$(M - H^+)^-$			84^j		50	44							
$CH_2{=}C(SiMe_3)OCH_2Bu^t$	$CH_2{=}\bar{C}OCH_2Bu^t$			100		67	62							
$MeCOCH_2Bu^t$	$(M - H^+)^-$			26			4							
$CH_2{=}CHOPh$	$(M - H^+)^-$							1	1	1		0.5		
MeCOPh	$(M - H^+)^-$								33	84				

[a] Width of HC_2O^- peak at half height = 70 ± 2 V. [b] Width of HC_2O^- peak at half height = 72 ± 2 V. [c] Composite peak centred at *m*/*z* 43. Central Gaussian peak superimposed on dish-shaped peak, width of composite peak at half height = 175 ± 3 V. [d] Width of HC_2O^- peak at half height = 47 ± 2 V. [e] *m*/*z* 57, $(MeCOCH_2)^-$, width of peak at half height = 107 ± 2 V. [f] Composite peak centred on *m*/*z* 43, central Gaussian peak superimposed on dish-shaped peak, width of composite peak at half height = 166.5 ± 3 V. [g] *m*/*z* 57, $(MeCOCH_2)^-$, width of peak at half height = 108 ± 2 V. [h] *m*/*z* 43, in this case, the dish-shaped component is the only peak detected (route *A*, Scheme 4). Route *B* (Scheme 4) is either not operational, or alternatively is minor in comparison with route *A*. The reason for this observation is not apparent, but it is interesting that this scenario only occurs when R = Pr^i or Bu^t. [i] *m*/*z* 57, $(MeCOCH_2)^-$, width of peak at half height = 104 ± 2 V. [j] *m*/*z* 57 $(MeCOCH_2)^-$, width of peak at half height = 71 ± 2 V. [k] The loss of C_2H_2 indicates the presence of some $^-CH{=}CHOCH_2Bu^t$, formed from a minor amount of $CH(SiMe)_3{=}CHOCH_2Bu^t$.

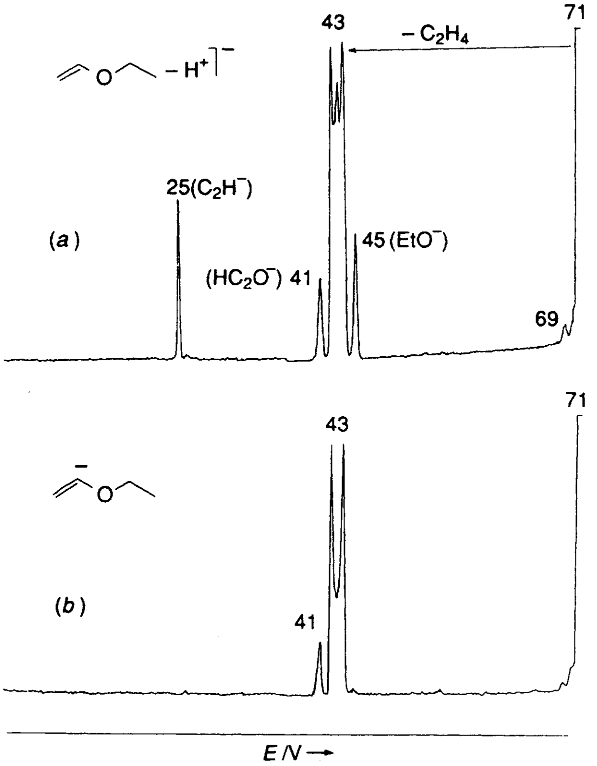


Figure 1. (*a*) Collisional-activation mass spectrum of the deprotonated ethyl vinyl ether. The peak width (at half height) of *m/z* 41 is 47.5 ± 2 V. The peak width (at half height) of the composite peak at *m/z* 43 is 177.5 ± 3 V. When a potential of +1 000 V is applied to the collision cell, about 50–60% of all peaks are shifted, indicating that this proportion of decompositions is occurring in the collision cell. Interestingly, for *m/z* 43, the shifted component (that produced by decomposition in the collision cell) shows a major Gaussian component, whereas the unshifted component (that produced by decomposition outside the collision cell) shows a major dish-shaped component. Thus route *A* is a more kinetically favoured process than route *B* (Scheme 4). (*b*) Collisional activation mass spectrum of $CH_2{=}\bar{C}OEt$ produced by the reaction $CH_2{=}C(SiMe_3)OEt + NH_2^- \longrightarrow CH_2{=}\bar{C}OEt + Me_3SiNH_2$.

at half height (70 ± 2 V). Thus the possibility of the Wittig rearrangement occurring must be seriously considered.

The ethyl vinyl ether spectra are shown in Figure 1. Again, there is the suggestion of a Wittig rearrangement since the peak widths at half height of the HC_2O^- peaks (*m/z* 41) in the spectra of $CH_2{=}\bar{C}OEt$ (Figure 1) and $(MeCOEt - H^+)^-$ (Table 1) are similar. However the spectra shown in Figure 1 are dominated by losses of ethene from the alkyl side chain. The spectra (Table 1) of the deuteriated derivatives demonstrate that the losses of ethene involve transfer of a methyl proton. The composite peak at *m/z* 43 in Figure 1(*a*) is composed of a dish-shaped peak produced by route *A* in Scheme 4 [*cf.* Figure 1(*b*)],* together with the central Gaussian component produced by proton transfer to the terminal vinylic position (route *B*, Scheme 4). Data contained in the legend to Figure 1 indicate that process *A* is favoured kinetically over process *B*. Similar fragmentations are observed in all cases where the allyl group is ⩾Et.

To date, we suspect the operation of the Wittig rearrangement for $CH_2{=}\bar{C}OMe$, and that it also occurs for $CH_2{=}\bar{C}OEt$, but that in the latter case, the rearrangement is suppressed by the more facile elimination of ethene from the side chain. In contrast, the Wittig rearrangement is substantiated in the spectra of $CH_2{=}\bar{C}OR$ (R = Pr^n, Bu^n, and CH$_2$Bu^t) by the occurrence of pronounced peaks at *m/z* 57. The spectra of the butyl derivatives (Figure 2) are typical of such ions. The spectra are similar to those considered earlier with the exception of the pronounced peak at *m/z* 57 which is shown by MS/MS/MS

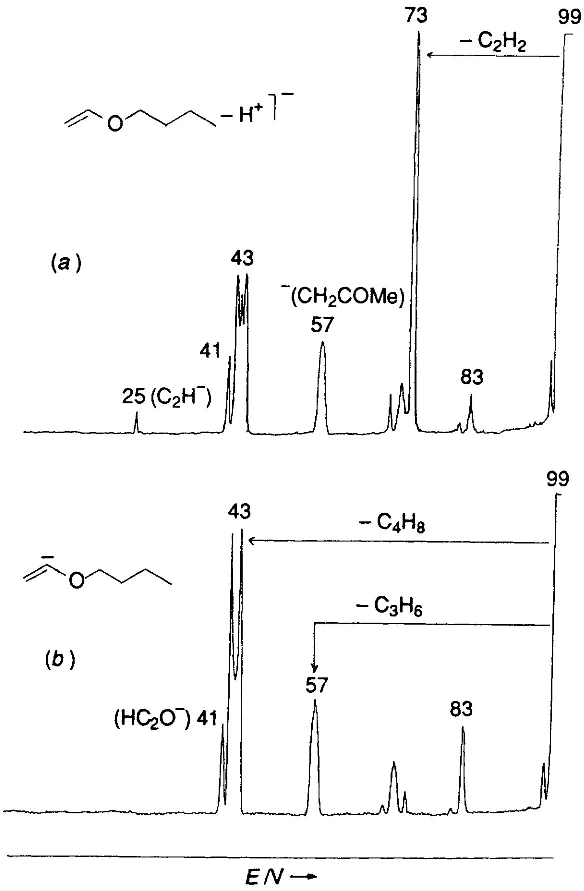
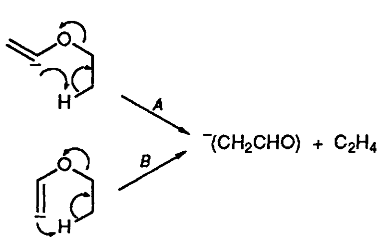


Figure 2. (*a*) Collisional activation mass spectrum of deprotonated n-butyl vinyl ether. The peak width (at half height) of *m/z* 57 is 103.5 ± 2 V. When a potential of + 1 000 volts is applied to the collision cell, only 10% of *m/z* 57 is shifted, indicating that only 10% of the decompositions occur inside the collision cell. Thus 90% of all decompositions are occurring outside the collision cell: this will be due to a combination of unimolecular dissociations and collision-induced dissociations (in the vicinity of the cell: caused by leakage of collision gas from the cell). The fact that *m/z* 57 may be formed by *unimolecular* dissociation means that the Wittig process (together with the subsequent decomposition) is a facile process in this case. (*b*) Collisional activation mass spectrum of $CH_2{=}\bar{C}OBu^n$ produced by the reaction $CH_2{=}C(SiMe_3)OBu^n + NH_2^- \longrightarrow CH_2{=}\bar{C}OBu^n + NH_3$.



Scheme 4.

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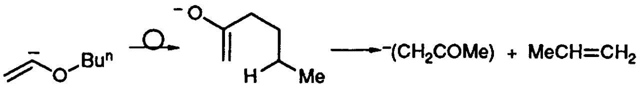
* Wide dish-shaped peaks are also produced by analogous losses of alkenes from other even-electron negative ions (*e.g.* ketone enolates,[14] alkyl amides,[15] and ethers [16]), and are often associated with reactions with considerable reverse activation energies.

Table 2. Experimental data for trimethyl vinyl alkyl ethers.[a]

Compound	Yield (%)	C B.p./°C	δ_H (60 MHz)
CH_2=C($SiMe_3$)OMe	91	103–104 (760 mmHg)	0.10 (9 H, s), 3.51 (3 H, s), 4.29 (1 H, d, *J* 2.0 Hz), 4.60 (1 H, d, *J* 2.0 Hz)
CH_2=C($SiMe_3$)OEt	84	137–138 (760 mmHg)	0.10 (9 H, s), 1.14 (3 H, t, *J* 7.0 Hz), 3.57 (2 H, q, *J* 7.0 Hz), 4.14 (1 H, d, *J* 1.8 Hz), 4.42 (1 H, d, *J* 1.8 Hz)
CH_2=C($SiMe_3$)OBu	76	97–99 (73 mmHg)	0.08 (9 H, s), 1.05–1.90 (7 H, m), 3.83 (2 H, t, *J* 7.0 Hz), 4.22 (1 H, d, *J* 2.0 Hz), 4.55 (1 H, d, *J* 2.0 Hz)
CH_2=C($SiMe_3$)OCH_2Bu^t	77	62–64 (48 mmHg)	0.14 (9 H, s), 0.96 (9 H s), 3.28 (2 H, s), 4.24 (1 H, d, 2.0 Hz), 4.56 (1 H, d, *J* 2.0 Hz)

[a] All these compounds hydrolyse readily and are unstable to air. Thus they were not submitted for elemental analysis. For CH_2=C($SiMe_3$)OMe, $M^{+\cdot}$ = 130.0809; $C_6H_{14}SiO$ requires 130.0810. The other compounds showed only low mass ions in their positive ion mass spectra: $M^{+\cdot}$ and/or $(M - Me^{\cdot})^+$ ions were absent.

data[*] to correspond to the acetone enolate ion $^-(CH_2COMe)$.[†] There is no way that the acetone enolate ion can arise directly from deprotonated butyl vinyl ether, thus the parent ion must rearrange prior to or during decomposition. The final evidence is given by the experimental observation that the *m*/*z* 57 peaks in the spectra of $CH_2=\bar{C}OBu^n$ and $(MeCOBu^n - H^+)^-$ have the same peak shape, including, within experimental error, the same peak width at half height (104 ± 2 V). Wittig rearrangement thus occurs as shown in Scheme 5 with the

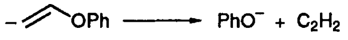


(5)

Scheme 5.

rearrangement product (5) undergoing the characteristic[13] ketone enolate rearrangement to yield $^-(CH_2COMe)$. This enolate rearrangement can only occur if the alkyl side chain has at least three carbon atoms in a 'straight' chain, with C-3 bearing at least one hydrogen.[14] Thus *m*/*z* 57 is observed when R = Pr^n, Bu^n, and *neo*pentyl, but not when R = Pr^i or Bu^t (Table 1, Figure 2).

Finally, if the Wittig reaction occurs at all for deprotonated phenyl vinyl ether, then it is very minor. The dominant reaction involves the formation of PhO^- and this is likely to occur mainly from the β-vinyl carbanion (Scheme 6).



Scheme 6.

In conclusion, it is proposed that the Wittig rearrangement shown in Scheme 2 occurs for all deprotonated alkyl vinyl ethers. However, the Wittig rearrangement is often not the dominant process; it generally competes unfavourably with elimination of an alkene from the alkyl side chain of the deprotonated ether.

Experimental

Full experimental details of the ZAB 2HF spectrometer[18] have been given previously.[14] The specific conditions are: the collisional ionization slit in the source, ion source temperature 150 °C, electron energy 70 eV, and accelerating voltage 7 kV. All ethers were introduced through the septum inlet which was maintained at 150 °C. The source pressure of substrate was 5×10^{-7} Torr (1 Torr = 133.322 Pa). The deprotonating agent (and desilylating agent) was NH_2^- (from NH_3, source pressure of NH_3 = 1×10^{-5} Torr). The estimated total source pressure was 10^{-1} Torr. Helium was used as the collision gas in the second collision cell. The measured pressure was 2×10^{-7} Torr, producing a 10% reduction in the main beam and corresponding essentially to single collision conditions. The electric sector scan mode was used. Peak widths at half height are a mean of ten individual scans, and (in general) are correct to within ±2 V.

All vinyl ethers were prepared by a standard method.[19] All ketones were commercial samples, except for neopentyl methyl ketone which was prepared by a reported method.[20]

The Trimethylsilyl Vinyl Alkyl Ethers.—General procedure. t-Butyl-lithium (1.70 mol dm^{-3} in pentane, 10 cm^3) was added to a stirred solution of alkyl vinyl ether (20 mmol) in anhydrous tetrahydrofuran (60 cm^3) at −78 °C under nitrogen. The mixture was allowed to warm to −25 °C and maintained at that temperature for 2 h. The mixture was then cooled to −78 °C and trimethylsilyl chloride (2.35 g) was added, the mixture was stirred for 3 h, allowed to warm to 20 °C, filtered under anhydrous nitrogen gas and the filtrate distilled through a 30 cm column of glass helices. All these compounds are readily hydrolysed and must be kept under a N_2 atmosphere.

Acknowledgements

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[*] The MS/MS/MS spectra were determined by forming the ion in the first field-free region, focussing it using the magnetic field and then recording the collisional activation and charge reversal[17] mass spectra in the conventional manner (see the Experimental). The spectra obtained were weak, with peaks of small abundance (< 10%) lost in baseline noise, but clearly identify *m*/*z* 57 as $^-(CH_2COMe)$: *viz* [*m*/*z* (relative abundance)]. CA MS/MS/MS: 56 (100), 41 (20). CR MS/MS/MS: 55 (10), 43(60), 42 (100), 41 (20), 39 (50), 29 (40), 27 (40), 26 (15), 15 (10) (*cf.* ref. 16).

[†] Deprotonation of $MeCOBu^n$ yields $^-(CH_2COBu^n)$ and $(MeCOCHPr)^-$, ions which certainly equilibrate on collisional activation. The spectrum of $(MeCOBu^n - H^+)^-$ (Table 1) shows fragmentations originating from both enolate ions, but $^-(CH_2COMe)$ arises specifically from $^-(CH_2COBu^n)$.[14]

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