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Formation of two deprotonated forms of benzyl acetate and higher homologues: some unusual fragmentations

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Abstract

Deprotonation of RCO_2CH_2Ph (R = Me, Et, iso Pr) with HO^- in the gas phase yields the two $(M\text{-}H)^-$ ions $(R\text{-}H)^-\text{-}CO_2CH_2Ph$ and $RCO_2^-\text{-}CHPh$ which do not interconvert under conditions of collisional activation. When R = *tert* Bu, deprotonation forms the benzylic anion exclusively. Both anions undergo fragmentation following extensive rearrangement. The enolate anions $(R\text{-}H)\text{-}^-CO_2CH_2Ph$ lose CO_2 following a Claisen type rearrangement. The benzylic anion $RCO_2^-\text{-}CHPh$ undergoes two complex rearrangements, viz (i) a 1,2 Wittig type rearrangement yielding $(Ph)(R)CHO^-$ and CO, and (ii) loss of the elements of R. The latter reaction is not a simple cleavage of R·: deuterium labelling supports stepwise loss of [H· + (R-H)] and product ion studies suggest the reaction proceeds through the complex rearrangement pathway $RCO_2\text{-}^-CHPh \rightarrow RCOCH(Ph)O^- \rightarrow RCH(O^-)COPh \rightarrow [PhCOCHO]^{-\cdot} + H\cdot + (R\text{-}H)$. The last step may proceed via a cyclic radical anion/radical intermediate. (Int J Mass Spectrom 179/180 (1998) 61–66) © 1998 Elsevier Science B.V.

Keywords: Benzyl acetate $(M\text{-}H)^-$ anions; Rearrangements on collisional activation

Introduction

We have recently reported a Wittig type rearrangement of deprotonated benzyl esters, viz. $RCO_2^-\text{-}CHPh \rightarrow (R)(Ph)(H)CH\text{-}O^- + CO$ (R = H, alkyl or aryl) [1]. When R = alkyl and when there is at least one hydrogen on the carbon adjacent to the carbonyl group, the neutral can be deprotonated to form two anions, an enolate species and a benzyl anion. Since we were interested in studying the reactions of the benzyl anion we used deuterated analogues: for example, we studied the $(M\text{-}D)^-$ ion of $CH_3CO_2CD_2Ph$. It was immediately apparent that the $(M\text{-}H)^-$ and the $(M\text{-}D)^-$ species of this neutral showed quite different fragmentations in their respective collision activation spectra. This in itself is of interest, since systems containing two centres with similar acidities (in this case ΔG^o_{acid} of each of the two centres is of the order of 1500–1530 kJ mol^{-1}) [2] often produce, on deprotonation, two carbanions which upon collisional activation, equilibrate via facile proton transfer [3]. In addition, there are several unusual fragmentations of these systems which were not reported earlier since they were not relevant to the Wittig rearrangement. We address these fragmentations in this article.

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Dedicated to Fulvio Cacace for his outstanding contributions in mass spectrometry and gas-phase ion chemistry.

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Table 1
Collision induced mass spectra of $(M\text{-}H)^-$ and/or $(M\text{-}D)^-$ ions from deuterium labelled analogues of RCO_2CH_2Ph and from PhCOCH(*tert*-Bu) OH

Neutral	Parent	Spectrum [mass (loss or formation) abundance]
$CH_3CO_2CD_2Ph$	$(M\text{-}H)^-$	150(H·)100, 109(CH_2CO)22, 107(CO_2)11, 77(Ph^-)8, 41(C_2HO^-)25.
	$(M\text{-}D)^-$	149(H·)100, 122(CO)15, 106(CH_3CHO)6, 105(CH_3CDO)12, 77(Ph^-)6, 43(PhCHO)3.
$CD_3CO_2CH_2Ph$	$(M\text{-}D)^-$	150(H·)100, 107(CD_2CO, CO_2)20, 77(Ph^-)5, 42(C_2DO^-)40.
	$(M\text{-}H)^-$	151(H·)100, 124(CO)12, 108(CO_2)4, 105(CD_3CHO)11, 77(Ph^-)5, 46(PhCHO)2.
$EtCO_2CD_2Ph$	$(M\text{-}H)^-$	164(H·)100, 121(CO_2)10, 109(MeCHO)11, 77(Ph^-)4, 55(MeC_2O^-)15.
	$(M\text{-}D)^-$	163(H·)100, 135(CO)10, 120(CO_2)1, 106(EtCHO)15, 105(EtCDO)20, 77(Ph^-)18, 57($EtCO^-$)5, 55(MeC_2O^-)1.
*tert*BuCO_2CH_2Ph	$(M\text{-}H)^-$	190(H·)5, 163(CO)12, 134(C_4H_9)100,[a] 105(*tert*-BuCHO)12, 77(Ph^-)6.
*tert*BuCO_2CD_2Ph	$(M\text{-}D)^-$	191(H·)98, 164(CO)15, 135(C_4H_9)100, 106(*tert*BuCHO)8, 105(*tert*BuCDO)12, 77(Ph^-)8.
$(CD_3)_3CCO_2CH_2Ph$	$(M\text{-}H)^-$	199/198[b](H·/D·)58, 163(CO)28, 134(C_4D_9)100, 105(C_4D_9CHO)12, 77(Ph^-)6.
PhCOCH(*tert*-Bu)(O^-)[c]		190(H·)5, 163(CO)11, 134(C_4H_9)100,[d] 105(*tert*-BuCHO)11, 77(Ph^-)5.

[a] Peak width at half height of *m/z* 134 = 30.1 ± 0.2 V.

[b] Unresolved

[c] Formed in the ion source by the S_N2(Si) reaction between HO^- and PhCOCH(*tert*-Bu) ($OSiMe_3$).

[d] Peak width at half height of *m/z* 134 = 30.2 ± 0.2 v.

Experimental

HO^- [CID and charge reversal (CR)] NICI MS/MS data were obtained with a reverse sector VG ZAB 2HF instrument [4]. Full details of the operation of the instrument have been given previously [5,6]. Specific details are as follows: the chemical ionisation slit was used in the ion source, the ionising energy was 70 eV, the ion source temperature was 150°, and the accelerating voltage 7 kV. All samples were introduced into the ion source using the septum inlet which was heated to 150°C. The measured source pressure of sample was typically 5×10^{-7} Torr. Deprotonation was effected by HO^- (from H_2O, measured source pressure 1×10^{-5} Torr) for all compounds except those labelled with deuterium α to the carbonyl group. In these cases, DO^- (from D_2O) was used. The $(M\text{-}H)^-$ [or $(M\text{-}D)^-$] ion was focussed using the magnet, fired through the second collision cell which contained argon [measured pressure outside the cell, 2×10^{-7} Torr (giving a 10% reduction in the ion beam signal, equivalent to single collision conditions)], and MS/MS data were obtained by scanning the electric sector. Charge-reversal spectra [7] were determined in a similar manner except that the voltage of the electric sector is reversed to allow the transmission of positive ions. Peak width measurements are an average of ten measurements.

ortho-xylene, 1-phenylpropane, phthalaldehyde, and phenylglyoxal were commercial samples. The acyloin PhCOCH(*tert*-Bu)(OH) was made by a standard procedure [8], and converted to the O-trimethyl silyl derivative using trimethylsilyl chloride and triethylamine in dimethylformamide [9]. The unlabelled benzylacetate and higher homologues were made by a standard technique [10]. D_2-benzyl acetate and higher homologues (RCO_2CD_2Ph) were made from $PhCD_2OH$ and the appropriate acid chloride by a standard technique ($D_2 > 99\%$) [10]. Benzyl D_3-acetate was made from D_3-acetyl chloride and benzyl alcohol ($D_3 > 99\%$) [10]. The D_9 *tert*-butyl ester [$(CD_3)_3CCO_2CH_2Ph$] ($D_9 > 99\%$) was made by a standard route from D_9 pivaloyl chloride [11].

Results and discussion

The collision induced tandem mass spectra (MS/MS) of $(M\text{-}H)^-$ and $(M\text{-}D)^-$ ions derived from deuterium labelled benzyl acetate and higher homologues are listed in Table 1. The spectra of the

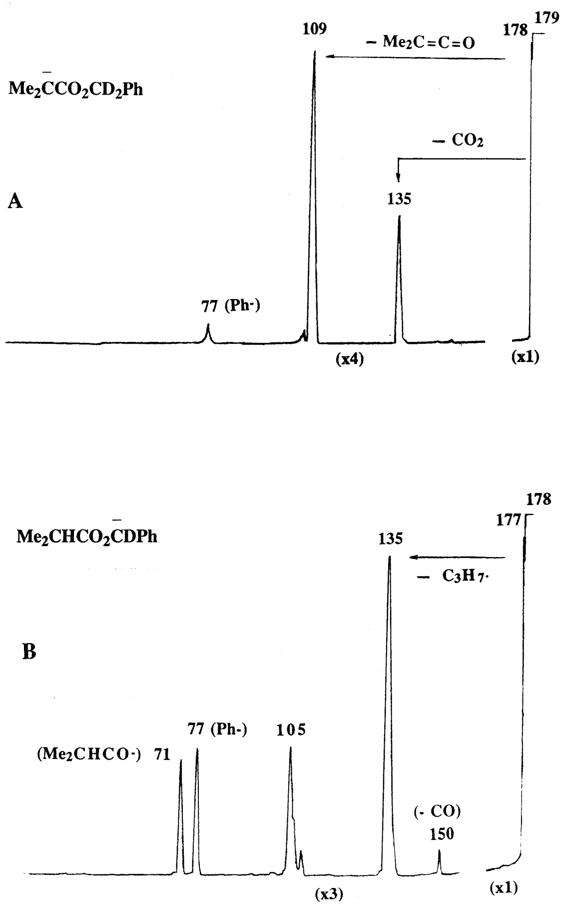


Fig. 1. Collision induced tandem mass spectra (MS/MS) of (A), the (M-H)$^-$ion, and (B), the (M-D)$^-$ ion of $Me_2CHCO_2CD_2Ph$. VG ZAB 2HF instrument. For experimental conditions see the Experimental section.

(M-H)$^-$ and (M-D)$^-$ ions of *iso* $PrCO_2CD_2Ph$ are recorded in Fig. 1 to demonstrate the nonequilibration of the enolate and benzylic anions, and to illustrate the two processes with which we will specifically deal in this article; namely, loss of CO_2 from the enolate anion, and loss of the alkyl group from the benzylic anion.

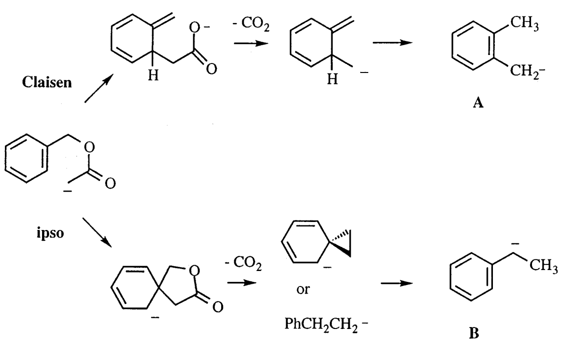
Losses of CO_2 from enolate anions

The spectra of all of the enolate species shown in Table 1 and Fig. 1 show competitive losses of carbon dioxide and a substituted ketene. Loss of ketene is the characteristic fragmentation of an enolate anion of a simple acetate, but loss of carbon dioxide is not observed for such a system [12]. This must mean that loss of CO_2 is kinetically unfavourable even though the thermodynamics are favourable (in contrast, loss of ketene is thermodynamically unfavourable but kinetically favourable), e.g. for the enolate anion of phenyl acetate, the following enthalpies are calculated using Benson's rules and known electron affinities [13]:

$$[{}^-CH_2CO_2Ph \rightarrow CH_2CO + PhO^- \qquad (\Delta H = +50\ kJ\ mol^{-1})]$$

$$[{}^-CH_2CO_2Ph \rightarrow CO_2 + PhCH_2^- \qquad (\Delta H = -130\ kJ\ mol^{-1})]$$

The benzyl group must be a prerequisite for the observed loss of CO_2 in these systems since this loss is not observed for alkyl or phenyl esters. There are two mechanisms which might rationalise this loss of CO_2. These are summarised in Scheme 1 for the prototypical case of benzyl acetate. The first is a Claisen type rearrangement, and an analogous gas-phase rearrangement involving the allyl system Ph-${}^-CHCO_2CH_2CH{=}CH_2$ has already been reported [14]. The initially formed product ion of such a rearrangement should transform to the more thermodynamically stable deprotonated *ortho*-xylene **(A)**. The second mechanism involves an *ipso* nucleophilic substitution: mechanisms of this type have also been reported [15,16]. The initially formed product ion of



Scheme 1

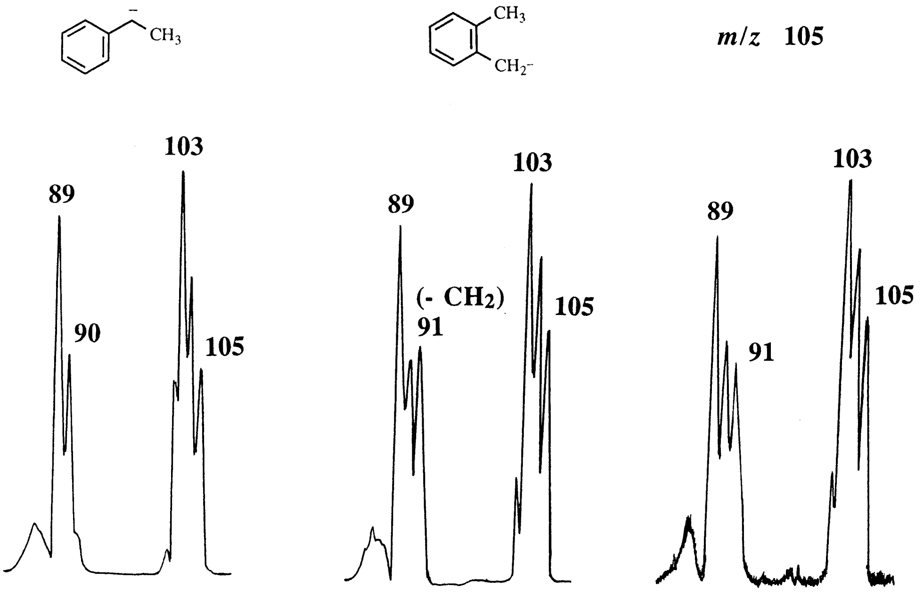


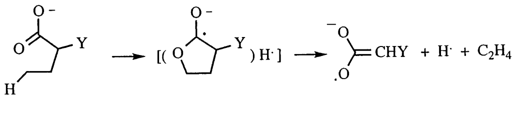
Fig. 2. The regions *m/z* 105–85 of the charge reversal (positive ion) mass spectra of the (M-H)$^-$ ions derived from (i) ethylbenzene and (ii) *ortho*-xylene, and the fragment ion *m/z* 105 from the (M-H)$^-$ species of $MeCO_2CH_2Ph$. VG ZAB 2HF mass spectrometer in charge reversal mode [7].

the *ipso* reaction is either the homobenzyl anion or the spiro[2,5]octadienyl anion (see Scheme 1), each of which is known to transform to the more stable methyl benzyl anion **(B)** [16].

In principle, we should be able to identify the product anion of a reaction from a consideration of its collisional activation and charge reversal (positive ion) mass spectra. However the collisional activation spectra of **A** and **B** are not diagnostic: each shows loss of a hydrogen atom as the major process. The charge reversal spectra of **A** and **B** are similar, but they may be distinguished by one feature. We have observed before that the charge reversal spectra of RCH_2^- species show characteristic loss of CH_2 from the parent cation [17]. This feature can be seen by comparison of the partial charge reversal spectra of **A** and **B** (Fig. 2). The source formed peak at *m/z* 105 from deprotonated benzyl acetate is a mixture of $C_8H_9^-$ and $C_6H_5CO^-$ (cf. Table 1). Of these two ions, only $C_8H_9^+$ can lose 14 Da, and only if a CH_2 unit is present. The appropriate portion of the charge reversal spectrum of *m/z* 105 from deprotonated benzyl acetate is shown in Fig. 2. The observed loss of CH_2 in consistent with the formulation of the product ion as **A**, thus supporting the operation of the Claisen type rearrangement shown in Scheme 1.

Loss of the alkyl group R from RCO_2^- CHPh

The data in Table 1 and Fig. 1 show that for the series R = Me, Et, *iso* Pr and *tert* Bu, loss of R from initially formed RCO_2-$^-$CHPh is not observed when R = Me, is minor for Et, is pronounced for *iso* Pr (Fig. 1) and is the base peak of the spectrum when R = *tert* Bu. We have encountered similar scenarios before, and have shown by deuterium labelling in such cases, that when R ≥ Et, the reactions do not involve loss of the radical R but stepwise loss of [H· + (R-H)]. The reactions may be rationalised as



Scheme 2

Table 2
Product ion studies on *m/z* 134 from *tert*-BuCO$_2$-$^-$CHPh

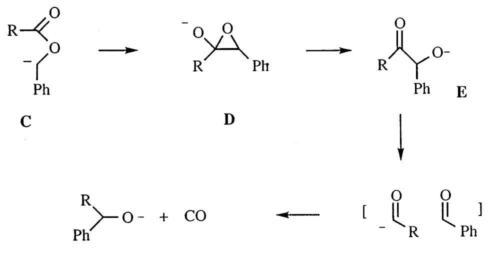
Precursor	Mode	Spectrum
		CA [mass (loss or formation) abundance] CR [mass (abundance)]
m/z 134	CA	133(H·)85, 105(CHO·)100, 77(Ph$^-$)42
	CR	134(13), 133(6), 105(100), 104(53), 89(35), 77(95), 63(38), 51/50(65), 39/38(22), 29(12)
$[PhCOCHO]^{-\cdot}$	CA	133(H·)90, 105(CHO·)100, 77(Ph$^-$)45
	CR	105(100), 104(53), 89(32), 77(92), 63(33), 51/50(62), 39/38(18), 29(14)
[*o*-OHC-C$_6$H$_4$-CHO]$^{-\cdot}$	CA	133(H·)45, 105(CHO·)100
	CR	134(46), 133(100), 118(15), 105(83), 89(16), 77(42), 63(24), 51/50(55), 39/38(18), 29(8)

proceeding via a stabilised cyclic radical anion intermediate [18]. A particular example is shown in Scheme 2 for the loss of the elements of C_2H_5 from a substituted butyrate anion (Y = H, alkyl, or aryl) [18].

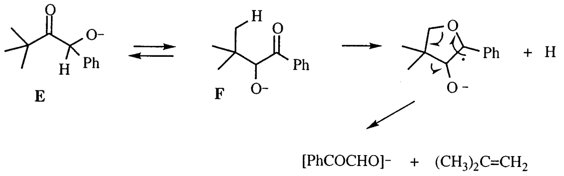
If a sequential process is operational in the current system, and if the loss of H· occurs in the rate determining step of the reaction, there will be a deuterium kinetic isotope effect for this process. In order to investigate this, we have compared the spectra of Me$_3$CCO$_2$-$^-$CHPh and (CD$_3$)$_3$CCO$_2$-$^-$CHPh (Table 1). Although this is purely a qualitative comparison, it is clear from the data listed in Table 1 that there is a significant deuterium isotope effect accompanying the loss of C_4H_9, e.g. the relative abundance ratios for losses of C_4H_9 and CO are 100:12 from the unlabelled anion, with the corresponding ratio for the losses of C_4D_9 and CO from the labelled analogue being 100:28, suggesting an isotope effect greater than two.

The structure of the product ion *m/z* 134 formed by loss of the elements of R is determined as follows. The collisional activation and charge reversal (positive ion) spectra of the source formed product ion *m/z* 134 are recorded in Table 2. Both the negative ion and charge reversal spectra of this species show losses of CHO· and (CHO· + CO), with the positive ion spectrum, in addition, exhibiting the loss sequence (CHO· + CO + C_2H_2). These data suggest that *m/z* 134 is $[PhCOCHO]^{-\cdot}$, a proposal supported by the spectra of the authentic radical anion $[PhCOCHO]^{-\cdot}$ (Table 2). (The charge reversal spectrum of *m/z* 134 is very similar to that of $[PhCOCHO]^{-\cdot}$ except that it shows a small parent cation recovery signal not observed for $[PhCOCHO]^{-\cdot}$. We first thought that this may be due to a minor contribution of the phthalaldehyde radical anion, but the data in Table 2 exclude that possibility. Perhaps the parent cation corresponds to PhCH(O·)-$^+$C = O, pointing to a minor contribution of PhCH(O·)-$^-$C = O in *m/z* 134?)

So far, we know that the loss of the elements of R involve transfer or loss of H in the rate determining step, and that the product ion of the reaction is $[PhCOCHO]^{-\cdot}$. What is the structure of the ion which is undergoing this reaction? At this stage it is necessary to refer back to the mechanism of the 1,2-Wittig rearrangement (Scheme 3) [1] as we need to consider some of the species in this rearrangement sequence with reference to the loss of R. The reaction sequence commences with the parent benzyl anion **C**, which cyclises to the epoxide **D** which ring opens to the keto-alkoxide **E**. Species **E** then undergoes a 1,2-Wittig type rearrangement to yield the product alkoxide anion together with neutral carbon monoxide [1]. Does loss of R occur from **C**, **D** or **E**? The loss of R cannot be a reaction of **C**, since (i) simple esters do not undergo such losses [3] (in particular, *tert* Bu CO$_2$-$^-$CHCO$_2$Me does not lose *tert* Bu· at all [19]), and (ii) even if R is lost, such a process cannot produce $[PhCOCHO]^{-\cdot}$. Similarly, neither **D** nor **E** can produce $[PhCOCHO]^{-\cdot}$ directly.



Scheme 3



Scheme 4

Since **C** to **E** are not direct precursors for loss of R, we propose the loss occurs from PhCOCH(R)(O^-) [**F** (R = *tert* Bu) in Scheme 4]. The species **F** may be formed from **E** by 1,2 H^- transfer (a facile process analogous to an acyloin rearrangement [20]), and a possible mechanism to explain the sequential loss of $H^{\cdot}$ + (R-H) from **F** is shown in Scheme 4 for R = *tert*-Bu. We have independently synthesised Ph-COCH (*tert*-Bu)O^- **(F)**: the spectrum is recorded in Table 1. The loss of the elements of C_4H_9 produces the base peak in the spectrum and the width at half height of the [(M-H)-$^-C_4H_9$] peak is the same (within experimental error) as that of the corresponding peak in the spectrum of *tert*-BuCO_2-CHPh. This supports the proposal that the loss of the elements of C_4H_9 originate from **F**. [The observation that the spectrum of **F** also shows loss of CO (the Wittig rearrangement) indicates that **E** and **F** interconvert under the reaction conditions.]

In conclusion, we propose that the loss of CO_2 from (R-H)-$^-CO_2CH_2$Ph occurs via a Claisen rearrangement, and the loss of the elements of R from RCO_2-$^-$CHPh involves stepwise loss of [H· + (R-H)] from PhCOCH(R)O^- following a complex rearrangement pathway involving four intermediates.

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