The collision induced loss of carbon monoxide from deprotonated benzyl benzoate in the gas phase. An anionic 1,2-Wittig type rearrangement

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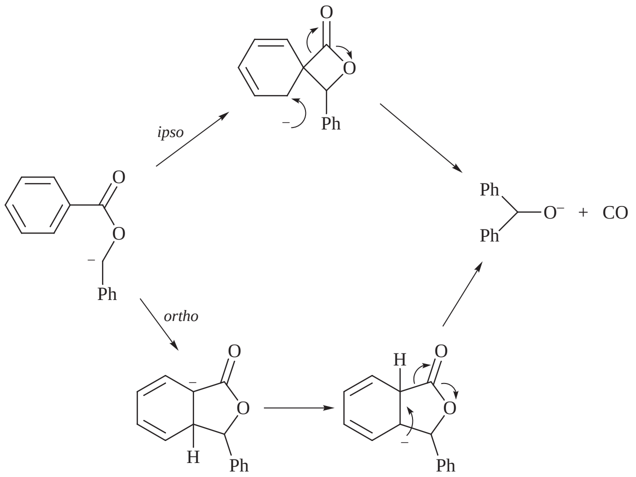
The ion $PhCO_2$–^-CHPh, upon collision activation, undergoes competitive losses of CO and CO_2 of which the former process produces the base peak of the spectrum. Product ion and substituent effect (Hammett) studies indicate that $PhCO_2$–^-CHPh cyclises to a deprotonated hydroxydiphenyloxirane which ring opens to $PhCOCH(O^-)Ph$. This anion then undergoes an anionic 1,2-Wittig type rearrangement {through [$PhCO^-$ (PhCHO)]} to form Ph_2CHO^- and CO. The mechanism of the 1,2-rearrangement has been probed by an *ab initio* study [at MP4(SDTQ)/6-31++G(d,p) level] of the model system $HCOCH_2O^- \longrightarrow MeO^- + CO$. The analogous system RCO_2–^-CHPh (R = alkyl) similarly loses CO, and the migratory aptitudes of the alkyl R groups in this reaction are $Bu^t > Me > Et \sim Pr^i$). This trend correlates with the order of anion basicities (*i.e.* the order of ΔG°_{acid} values of RH), supporting the operation of an anion migration process. The loss of CO_2 from $PhCO_2$–^-CHPh yields Ph_2CH^- as the anionic product: several mechanistic scenarios are possible, one of which involves an initial *ipso* nucleophilic substitution.

Introduction

As part of a study of the gas phase Cannizzaro reaction, we reported that deprotonated benzyl benzoate, upon collisional activation, eliminates carbon monoxide to form deprotonated diphenylmethanol.[1] This must involve some form of rearrangement.[cf.2] There are a number of possible mechanistic scenarios which need to be considered: these are summarised in Schemes 1 and 2. Both pathways shown in Scheme 1 involve initial nucleophilic attack of the benzylic anion to a phenyl ring. In contrast, both mechanisms shown in Scheme 2 involve a 'Wittig' type 1,2-migration (where Ph migration and CO elision are synchronous) in the last step, but they differ in the way the key 'Wittig' precursor species is formed.



Scheme 1

This paper provides experimental evidence which suggests that the cyclisation–'Wittig' rearrangement best accounts for the loss of CO from $PhCO_2$–^-CHPh.

Results and discussion

The reaction between DO^- and $PhCO_2CD_2Ph$ gives an $(M - D)^-$ ion exclusively, while the analogous reaction between HO^- and $C_6D_5CO_2CH_2Ph$ yields only an $(M - H)^-$ ion. The collisional activation tandem mass spectrum (CID MS–MS) of the latter parent anion is recorded in Fig. 1. In addition to the pronounced loss of CO, there is also a rearrangement peak corresponding to loss of CO_2. We will discuss each of these rearrangements seriatim.

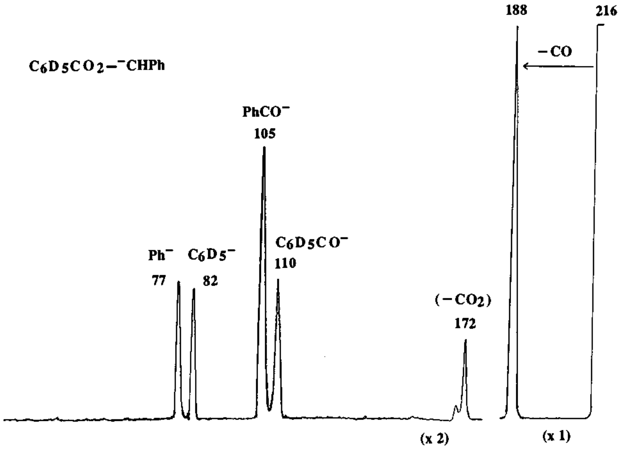
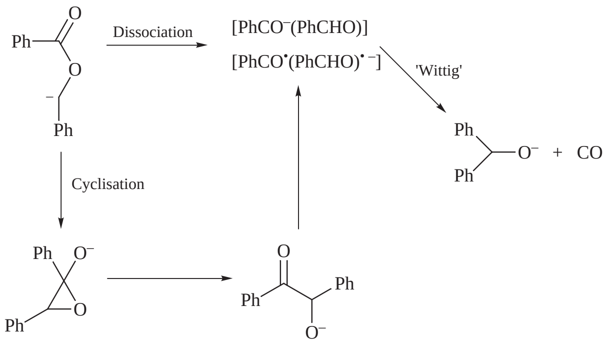


Fig. 1 CID mass spectrum (MS–MS) of $C_6D_5CO_2$–^-CHPh. VG ZAB 2HF mass spectrometer. For details see Experimental section.



Scheme 2

Table 1 Mass spectra of $Ar^1CO_2–^-CHAr^2$

Substituents			Relative intensity						
Ar^1	Ar^2	σ value	$[(M - H)^- - CO]$	Ar^1CO^-	$[(M - H)^- - Ar^1CHO]$	$[(M - H)^- - CO_2)]$	Ar^{1-}	Ar^{2-}	$[(M - H)^- - Me^{\bullet}]$
p-MeO	H	−0.28	100	60	19	28	5	1	68
H	H[b]	0	100	33[a]	17[a]	8	6[b]	6[b]	
m-MeO	H	+0.10	100	35	15	25	6	2	60
p-F	H	+0.15	100	34	13	20	10	4	
m-F	H	+0.35	100	6	12	35	8	1	
m-CN	H	+0.61	100	4	6	20	18		
p-CN	H	+0.65	100	4		35	20		
H	*p*-MeO	−0.28	100	33	54	32	5	15	38
H	H[b]	0	100	33[a]	17[a]	8	6[b]	6[b]	
H	*m*-MeO	+0.10	100	11	23	17	4	14	26
H	*p*-F	+0.15	100	4	18	32	4	18	
H	*m*-F	+0.35	100	2	11	28	3	12	
H	*m*-CN	+0.61	100	1	7	24		22	
H	*p*-CN	+0.65	100	0.5	10	35		28	

[a] From Fig. 1. [b] $Ar^1 = Ar^2 = Ph$.

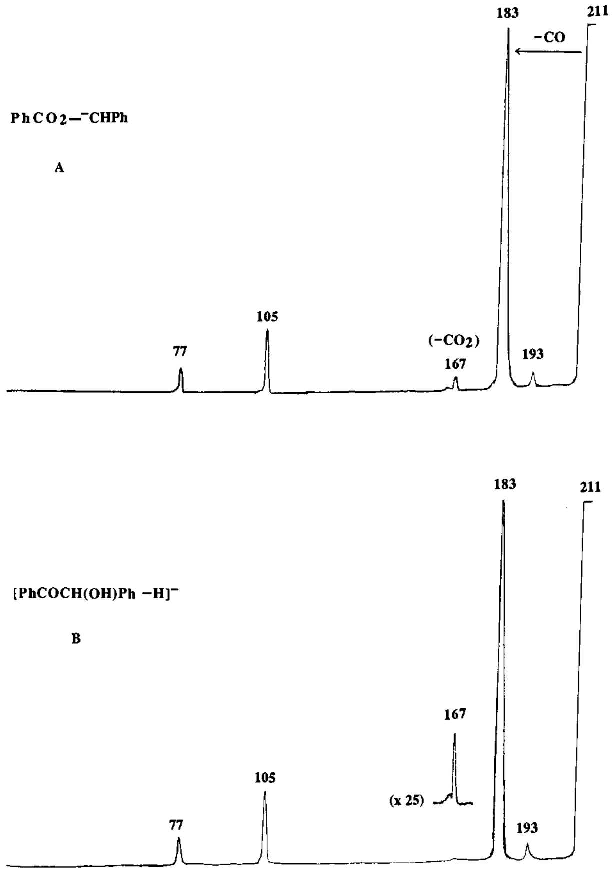


Fig. 2 CID mass spectra of (A) $PhCO_2–^-CHPh$, and (B) $[PhCOCH(OH)Ph - H]^-$. Peak widths at half height (A) −CO (31.7 ± 0.3); $-CO_2$ (35.4); (B) −CO (31.7), $-CO_2$ (23.5 ± 0.3 V).

(A) The loss of carbon monoxide from deprotonated benzyl benzoates

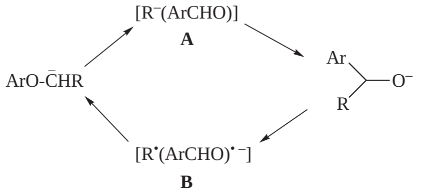
The mechanisms to be considered for the loss of CO are summarised in Schemes 1 and 2. The simplest way to commence this investigation is to consider the cyclisation–'Wittig' mechanism shown in Scheme 2: initial cyclisation through a deprotonated hydroxyoxirane system has ample precedent in the literature.[3–5] If the loss of CO follows the conversion of the parent anion $PhCO_2^-CHPh$ to $PhCOCH(O^-)Ph$, the spectra of both species should exhibit $[(M - H)^- - CO]$ ions and the peak widths at half height of these ions should be the same in the two spectra. The two mass spectra are shown, for comparison, in Fig. 2. The two spectra are similar, in particular, the peak widths at half height of the two $[(M - H)^- - CO]^-$ peaks are the same within experimental error (see legend to Fig. 2). The only difference noted in the two spectra concerns the $[(M - H)^- - CO_2]$ peaks. This peak is of smaller abundance in the spectrum of $[PhCOCH(OH)Ph - H]^-$ and the widths at half height of the peaks in the two spectra are significantly different (see legend to Fig. 2). This suggests that the losses of CO are arising *via* intermediates common to both $PhCO_2–^-CHPh$ and $[PhCOCH(OH)Ph - H]^-$, but that the situation concerning the losses of CO_2 from the two parent ions is more complex.

The experimental evidence outlined above suggests that the loss of CO from deprotonated benzyl benzoate is occurring *via* the cyclisation–'Wittig' process summarised in Scheme 2. Let us now investigate whether there is any evidence which favours (or disfavours) either of the *ipso* or *ortho* nucleophilic substitution mechanisms shown in Scheme 1. Such gas-phase rearrangements are not uncommon and examples have been reported before (*cf.* the *ipso* Smiles rearrangement and the competing *ortho* rearrangement[6,7]). We have investigated these aspects using a Hammett type substituent effect study. Different *meta* and *para* substituents were placed on each of the phenyl rings of the benzyl benzoate and the abundances of ions $[(M - H) - CO]^-$ were monitored as a function of the electronic nature (the Hammett σ value) of the substituent. It is necessary to be wary using Hammett studies in the gas phase, since there is often no inbuilt standard (or standard fragmentation) with which to compare the reaction under investigation. The following Hammett study is used only to indicate general trends. The abundance ratios of the major fragment ions in the spectra of a variety of ions of the general formula $Ar^1CO_2–^-CHAr^2$, together with known Hammett σ values[8] of the substituents used in this study, are summarised in Table 1.

A comparison of the abundances of $[(M - H) - CO]^-$ ions with those of either the Ar^1CO^- or $[(M - H) - Ar^1CHO]^-$ fragment ion (see Table 1), shows that the abundance of the rearrangement ion increases with an increase in σ (with an increase in electron withdrawing character) of the substituent on either ring. Consider now the *ipso* and *ortho* nucleophilic cyclisation mechanisms summarised in Scheme 1. In both cases, (i) if the ring cyclisation (the first step) is rate determining for the loss of CO from $Ar^1CO_2–^-CHAr^2$, then a higher value of σ^1 and a lower value of σ^2 will accelerate the ring cyclisation (*i.e.* increasing electron withdrawing character on Ar^1 will enhance the elecrophilicity at the carbon to which the nucleophile approaches, and increasing electron introducing character on Ar^2 will enhance the nucleophilicity of the attacking carbanion). Consider next, the second step (the 1,2-H transfer) of the *ortho* cyclisation mechanism (Scheme 1). Such a concerted

1,2-H transfer through a proton bound transition state is forbidden by the Woodward Hoffman rules: it has an activation barrier in the vicinity of 200 kJ mol^{-1} [9–11] and there are no recorded examples in the condensed phase of 1,2-H migration along a carbon side chain *via* carbanions.[12] However, if a 1,2-H transfer does operate, this step is likely to be rate determining. In such a situation, a lower value of σ^1 (*i.e.* making the reacting carbanion more basic) will increase the rate, and although the effect of σ^2 should be small, an increase in σ^2 will make the H of the breaking C–H bond more acidic, and marginally increase the rate. The final possibility is that where the final steps of both the *ipso* and *ortho* mechanistic proposals are rate determining (Scheme 1). A decrease in σ^1 will increase the electron density on the initial carbanion site thus increasing the rate, while an increase in σ^2 will stabilise the product alkoxide anion, thus effectively reducing the barrier to the transition state. None of the considered scenarios correlate with the experimental observation (that the abundance of the rearrangement ion is greater with a high value of σ^1 and a low value of σ^2). Thus we may eliminate the mechanistic scenarios proposed in Scheme 1, and return to the consideration of a 1,2-'Wittig' type mechanism.

The classical 1,2-Wittig rearrangement in solution is usually represented as shown in Scheme 3 (R is generally an alkyl group). The reaction is reported to be stepwise with the second step being rate determining.[13] There has been debate as to whether the intermediate is anion–neutral **A** or radical–radical anion **B**, but since the rates follow the migratory aptitudes of radicals in some cases, the radical–radical anion mechanism has been preferred.[14] However, the radical mechanism is not universally accepted.[15] The 1,2-Wittig reaction also occurs in the gas phase,[16,17] and an *ab initio* study of a model system ($^-$CH$_2$OMe ⟶ EtO$^-$), suggests an anionic pathway in which there is no discrete intermediate.[18]



Scheme 3

We know that the initial reaction pathway proceeds *via* an oxirane cyclisation–ring opening in the case of PhCO$_2$–$^-$CHPh (see Scheme 2): it is the mechanism of the phenyl migration which needs to be established. Thus we have carried out *ab initio* calculations [at MP4(SDTQ)/6-31++G(d,p) level][19] for the model system HCOCH$_2$O$^-$ (*i.e.* HCOCH$_2$O$^-$ ⟶ MeO$^-$ + CO. There are two anion rearrangement channels; no evidence is found for any reaction involving radical migration (*i.e.* both RHF and UHF calculations on the two intermediates shown in Fig. 3 give identical anionic structures). The first rearrangement channel is an unfavourable concerted reaction with a barrier of 310 kJ mol^{-1}. The geometry of the transition state is shown in Table 2. The second rearrangement pathway is the stepwise process summarised in Fig. 3, with details recorded in Table 2. There are a number of equilibrating cluster ions (separated in energy by less than 5 kJ mol^{-1}) on a plateau close in energy to the initial transition state. Two of these are shown in Fig. 3. The equilibrating clusters may undergo two reactions. The first is the dissociation process yielding HCO$^-$ and CH$_2$O (endothermic by 202 kJ mol^{-1}). The second process is the rearrangement. Once the second complex is formed, the system may proceed to the rearrangement products (MeO$^-$ and CO). The rearrangement process is inefficient because the reaction channel is narrow [*i.e.* the frequency factor (the pre Arrhenius *A* factor) is low], because reversion to reactant is more favourable than conversion to products across the flat energy plateau. The consequence of this is that the migration (second) step shown in Fig. 3 is likely to be rate determining.

The PhCO$_2$–$^-$CHPh system is too large for us to compute at an appropriate level using *ab initio* calculations, thus we have constructed a reaction coordinate diagram using Benson's rules[20] and known electron affinities[21] to estimate the energies of all stable species, and have used the results of the *ab initio* calculation on the model system as a guide to the barrier heights of the phenyl migration steps. These data are summarised in Fig. 4.

Let us now revisit the results of the Hammett study. Although it now seems likely that the final migration step is rate determining, let us consider the expected substituent effects for each of

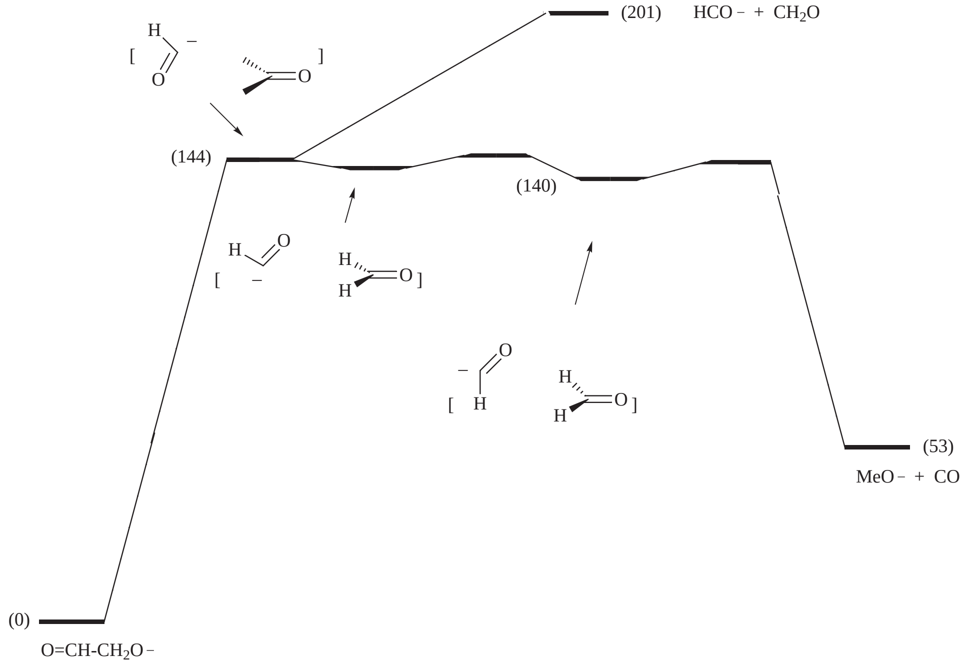
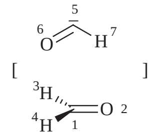


Fig. 3 Reaction coordinate energy diagram of the reactions O=CH–CH$_2$O$^-$ ⟶ HCO$^-$ + CH$_2$O and O=CH–CH$_2$O$^-$ ⟶ MeO$^-$ + CO. Gaussian 94. Geometries optimised at MP2(full)/6-31++G(d,p). Energies optimised at MP4(SDTQ)/6-31++G(d,p)//MP2(full)/6-31++G(d,p) level [zero point energy corrected (scaled 0.9)]. C–C distances as follows: transition state (2.842 Å), association complex 1 (2.960 Å), and association complex 2 (2.962 Å). For full data concerning energies and geometries see Table 2.

Table 2 Energies and geometries of transition states and intermediates shown in Fig. 3[a]

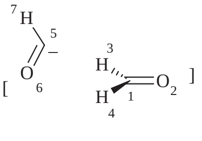
Reactant [O=CHCH$_2$O$^-$ (anti form)]:	−227.833 563 8 hartrees,	0 kJ mol^{-1}
Product (MeO$^-$ + CO):	−227.813 419 5,	+52.9
Product (HCO$^-$ + CH$_2$O):	−227.756 706 8,	+201.8

Transition state concerted



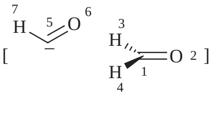
−227.833 563 8 hartrees +309.6 kJ mol^{-1}	C_1O_2	1.308 Å	$O_2C_1H_3(H_4)$	119.54°
	$C_1H_3(H_4)$	1.116	$H_3C_1H_4$	110.32
	C_5O_6	1.217	$O_6C_5H_7$	164.82
	C_1C_5	2.023	$O_6C_1H_3(H_4)$	76.45
	C_1O_6	2.661	$O_2C_1H_7$	86.48

Transition state stepwise



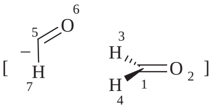
−227.778 559 5 hartrees +144.41 kJ mol^{-1}	C_1O_2	1.238 Å	$O_2C_1H_3(H_4)$	122.55°
	$C_1H_3(H_4)$	1.090	$H_3C_1H_4$	114.87
	C_5O_6	1.258	$O_6C_5H_7$	109.87
	C_5H_7	1.168	$C_5C_1H_3(H_4)$	62.62
	C_1C_5	2.842	$C_5C_1O_2$	150.17
	$O_6H_3(H_4)$	2.517		

Association complex 1



−227.778 660 5 hartrees +144.15 kJ mol^{-1}	C_1O_2	1.236 Å	$O_2C_1H_3(H_4)$	122.41°
	$C_1H_3(H_4)$	1.092	$H_3C_1H_4$	115.02
	C_5O_6	1.261	$O_6C_5H_7$	109.17
	C_5H_7	1.163	$H_3(H_4)C_1C_5$	62.50
			$C_5C_1O_2$	153.13
			$O_6C_1O_2$	128.18

Association complex 2



−227.780 315 5 hartrees +139.80 kJ mol^{-1}	C_1O_2	1.238 Å	$O_2C_1H_3(H_4)$	122.14°
	$C_1H_3(H_4)$	1.092	$H_3C_1H_4$	114.97
	C_5O_6	1.253	$O_6C_5H_7$	109.14
	C_5H_7	1.198	$H_3(H_4)C_1H_7$	58.73
	C_1O_6	2.344	$C_1O_6C_5$	107.15
	C_1C_5	2.964	$C_5C_1O_2$	147.18
	C_1H_7	2.582		

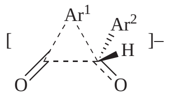
[a] Gaussian 94.[19] Geometries at MP2(full)/6-31++G(d,p). Energies at MP4 (SDTQ)6-31++G(d,p)//MP2(full)6-31++G(d,p), corrected for zero point energy (scaled 0.9).

the four steps shown in Fig. 4. Experimentally, we have determined that increasing the electron withdrawing effect of substituents on either Ar^1 or Ar^2 increases the abundance of the [(M − H) − CO]$^-$ ion (*i.e.* a larger k value with a high σ^1 and a low σ^2).

If step 1 is rate determining, the rate will increase with increasing σ^1 (increases the electrophilicity of the carbonyl carbon), and decreasing σ^2 (increases the nucleophilicity of the attacking carbanion). If step 2 is rate determining the rate will increase with decreasing σ^1 and increasing σ^2. If the dissociative step (step 3) of the 1,2-rearrangement is rate determining, the rate will increase with increasing σ^1 and decreasing σ^2. None of these scenarios conform to the experimental results.

Table 3 Mass spectra of RCO$_2$–$^-$CDPh

	Relative intensity					
R	[(M − H)$^-$ − CO]	RCO$^-$	−RCO^{2}D	−RCO$_2$H	Ph$^-$	[(M − H)$^-$ − R$^•$]
Me	100	14	74	24	32	8
Et	14	14	100	75	71	12
Pr^i	15	17	49	18	23	100
Bu^t	25	1.5	10	5	26	100



Migration

Migration step 4 may be represented as shown above. The expected electronic effects are as follows: (a) electron withdrawing effects (large σ^2) will assist the attack of the nucleophile at the carbonyl group of Ar^{2}CHO, and (b) there are two opposing substituent effects of Ar^1: *viz.* (i) electron withdrawing effects (large σ^1) will aid the dissociation of Ar^1–CO$^-$ to Ar^{1-} and CO, and (ii) electron introducing effects (small σ^1) will aid the attack of the nucleophilic Ar^{1-} at the carbonyl group of Ar^{2}CHO. The only scenario which conforms to the experimental results of the Hammett study (*i.e.* the rate increasing with increasing σ^1 and increasing σ^2) is that step 4 is rate determining with (a) and (b, i) being the major features affecting the rate. Thus the electronic effect of the substituent on the dissociation of Ar^{1}CO$^-$ to Ar^{1-} is more important than its effect on the nucleophilicity of Ar^{1-}.

Finally, we need to consider the possibility that the migration step is a radical reaction (*cf.* Scheme 3). There are several possible stepwise pathways and a concerted route to consider [from Ar^{1}COCH(O$^-$)Ar^2] but they all have one feature in common. If the migration of Ar$^{1•}$ to $^•$CH(Ar^2)(O$^-$) to yield Ar^{1}Ar^{2}CHO$^-$ is rate determining, the rate must increase with decreasing σ^1 and increasing σ^2. This is not in accord with experimental data. In addition, radical reactions are generally much less influenced by electronic effects than are ionic processes:[22] the substituent effects shown in Table 1 for loss of CO are pronounced.

We conclude that (a) the formation of Ph$_2$CHO$^-$ and CO from PhCO$_2$–$^-$CHPh occurs by the complex sequence shown in Fig. 4, (b) phenyl migration step 4 is rate determining and (c) there are two major factors influencing the rate of the phenyl rearrangement step, *viz.* the low probability of phenyl migration in comparison to (i) the back reaction, and (ii) the competing cleavage reaction (*i.e.* that yielding PhCO$^-$ + PhCHO).

(B) The loss of carbon monoxide from RCO$_2$–$^-$CHPh (R = alkyl)

We have described above (i) how there has been debate concerning whether the 1,2-Wittig rearrangement is a radical or anionic reaction, and (ii) that the loss of CO from PhCO$_2$–$^-$CHPh is best represented in terms of an anionic 1,2-Wittig type mechanism. What we wish to do now is to study a cognate system in which there is a reasonable possibility that the rearrangement step could involve a radical rather than an anion migration. To this end we have made a series of compounds RCO$_2$CD$_2$Ph [R = alkyl (Me, Et, Pr^i and Bu^t)]. Should the (M − D)$^-$ ions of these compounds lose CO, it is possible that the rearrangement may involve radical migration, since [RCO$^•$ (PhCDO)$^{•-}$] might partake in the reaction {*i.e.* in the case of [MeCO$^•$ (PhCHO)$^{•-}$], the electron affinities of MeCO$^{•}$[23] and PhCHO[24] are both close to 42 kJ mol^{-1}}.

The mass spectrum of the (M − D)$^-$ ion from MeCO$_2$-CD$_2$Ph is shown in Fig. 5, while the major fragmentations of all four of the (M − D)$^-$ ions are summarised in Table 3. The spectra show both [(M − H)$^-$ − CO] and RCO$^-$ ions (see Table 3

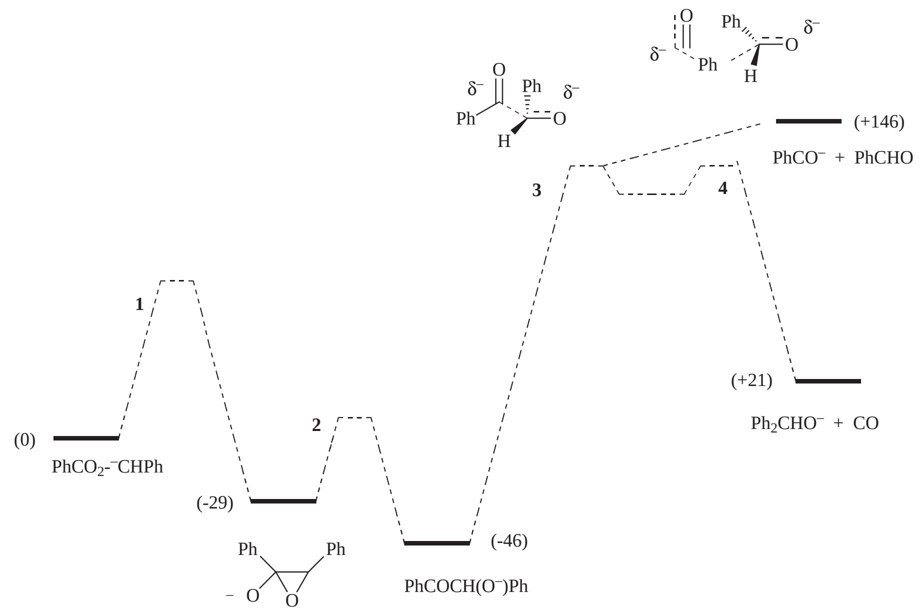


Fig. 4 Reaction coordinate energy diagram of the system $PhCO_2$– $^-CHPh \longrightarrow (Ph)_2CHO^-$ + CO. Energies calculated using Benson's rules[20] and estimated electron affinities.[21] Transition state energies for the final rearrangement reaction are those computed for Fig. 3.

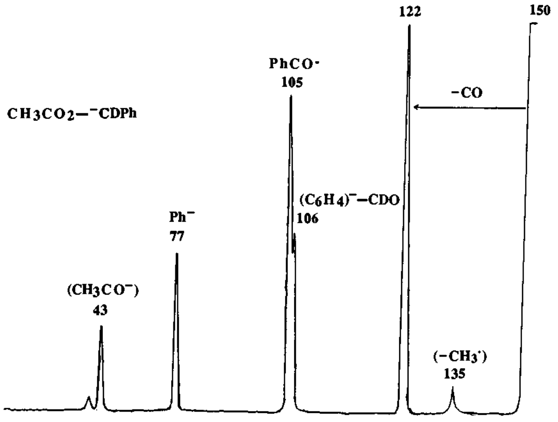


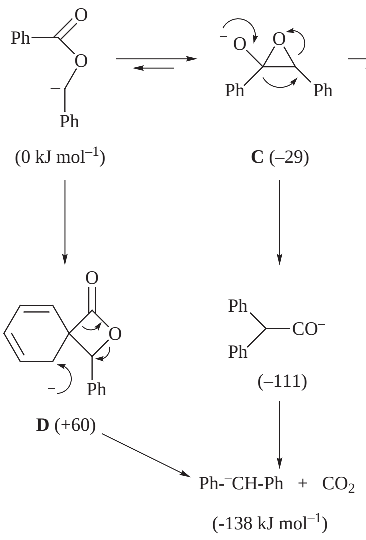
Fig. 5 CID mass spectrum (MS–MS) of $(CH_3CO_2CD_2Ph - D)^-$. VG 2HF mass spectrometer. For experimental details see Experimental section.

and Fig. 5, and *cf.* Fig. 4) and a comparison of the relative abundances of these peaks in the four spectra should give a qualitative indication of the relative probabilities of the rearrangement reactions in the four systems, *i.e.* the migratory trend of the alkyl groups. If it is a radical reaction, the migratory aptitudes should be $Bu^{t\bullet} > Pr^{i\bullet} > Et^\bullet > Me^\bullet$.[*cf.* 14] If the reaction is anionic, the gas-phase anion migratory aptitude should follow the ΔG°_{acid} value for the process $RH \longrightarrow R^- + H^+$ (the smaller the value, the higher the migratory aptitude). The ΔG°_{acid} values are as follows: CH_4 (1709 kJ mol^{-1}),[25] C_2H_6 (1724),[26] Me_2CH_2 (1722)[26] and Me_3CH (1701 kJ mol^{-1}).[26] Thus the theoretical thermodynamic gas-phase anion migration trend should be $Bu^{t-} > Me^- > Pr^{i-} > Et^-$. The data listed in Table 2 show the following trend in migratory aptitude: $Bu^t > Me > Et \sim Pr^i$, these data are thus consistent with an anion reaction.

(C) The loss of CO_2 from $PhCO_2$–^-CHPh

The spectra of both $PhCO_2$–^-CHPh and $[PhCOCH(OH)Ph - H]^-$ show loss of CO_2, the peak widths of these product peaks are different (see legend to Fig. 2), and the product peak is of smaller abundance in the spectrum of $[PhCOCH(OH)Ph - H]^-$. The Hammett study (see Table 1) does not indicate any particular trend, unlike the situation pertaining to the loss of CO. The CO_2 yields product ions in both spectra which show the characteristic fragmentations of the diphenylmethyl anion.[27]

There are two plausible mechanisms for the loss of CO_2 from $PhCO_2$–^-CHPh: these are summarised in Scheme 4, together with estimated Δ_fH° values for reactant, intermediates and products. The first possibility involves phenyl migration within the oxirane species **C** to form the diphenylacetate anion which then decarboxylates to form the diphenylmethyl anion. The second process is an *ipso* nucleophilic substitution to give **D** which then loses CO_2. Loss of carbon dioxide from $PhCOCH(O^-)Ph$ occurs specifically through **C**, since the $[(M - H) - CO_2]$ peaks in the spectra of $Ph_2CHCO_2^-$ and $[PhCOCH(OH)Ph - H]^-$ have the same width at half height (23.5 ± 0.3 V) {the $[(M - H) - CO_2]^-$ ion produces the only major daughter peak in the spectrum of $Ph_2CHCO_2^-$}. The peak width of the $[(M - H) - CO_2]^-$ peak from $PhCO_2$–^-CHPh (35.4 ± 0.3 V) is appreciably different from the widths of the corresponding peaks from $[PhCOCH(OH)Ph]^-$ and $Ph_2CHCO_2^-$ (both 23.5 ± 0.3 V). Thus the mechanism of CO_2 loss from $PhCO_2$–^-CHPh cannot occur exclusively *via* **C**. We propose that either the loss of CO_2 occurs (i) exclusively by an *ipso* mechanism through **D** (see Scheme 4), or (ii) the competitive pathways shown in Scheme 4 are both operative.



Scheme 4

Conclusions

Deprotonated benzyl benzoate undergoes competitive rearrangement reactions resulting in the losses of CO and CO_2. The rearrangement pathways are summarised in Scheme 2 and Scheme 4. Cyclisation of $PhCO_2{-}^{-}CHPh$ yields an energised deprotonated diphenylhydroxyoxirane which undergoes ring opening to form deprotonated deoxybenzoin which then dissociates *via* an anionic 1,2-Wittig type rearrangement to yield the diphenylmethoxide anion and carbon monoxide (Scheme 2). The loss of CO_2 from $PhCO_2{-}^{-}CHPh$ is more complex: this may occur exclusively by an *ipso* arrangement through **D**, or by two competitive losses through **C** and **D** (Scheme 4).

Experimental

Mass spectrometric methods

Collisional activation (CID) mass spectra (MS–MS) were determined with a VG ZAB 2HF mass spectrometer.[28] Full operating details have been reported.[29] Specific details were as follows: the chemical ionisation slit was used in the chemical ionisation source, the ionising energy was 70 eV, the ion source temperature was 100 °C, and the accelerating voltage was 7 kV. The liquid samples were introduced through the septum inlet with no heating [measured pressure of sample 1×10^{-6} Torr (1 Torr = 133.322 Pa)]. Solid samples were introduced *via* the direct probe with no heating. Deprotonation was effected for unlabelled compounds using HO^- (from H_2O: measured pressure 1×10^{-5} Torr). In the case of deuterated derivatives, DO^- (from D_2O) was used as the base. The estimated source pressure was 10^{-1} Torr. CID MS–MS data were obtained by selecting the particular anion under study with the magnetic sector, passing it through the collision cell, and using the electric sector to separate and monitor the product ions. Argon was used as collision gas in the second collision cell (measured pressure, outside the cell, 2×10^{-7} Torr), giving a 10% reduction in the main beam, equivalent to single collision conditions. Peak width measurements were performed with the instrument in MS–MS mode using the electric sector to scan the peak under study. The peak width (at half height), quoted in V, is a mean of ten individual experiments (the main beam peak width at half height under the instrumental conditions used was 6 V).

Ab initio calculations on stable anions for the model system $HCOCH_2O^- \longrightarrow MeO^- + CO$ were carried out using Gaussian 94.[19] Geometries were optimised at MP2(full)/6-31++G(d,p) level while energies were computed at the MP4(SDTQ)/6-31++G(d,p)//MP2(full)/6-31++G(d,p) level and corrected for zero point energies (scaled to 0.9). Full procedural details of such calculations have been reported.[30]

Benzyl benzoate, deoxybenzoin and diphenylacetic acid were commercial products.

Benzyl [α,α-$^2H_2$]benzoate. This was made by a standard procedure[31] from [α,α-$^2H_2$]benzyl alcohol and benzoyl chloride. Yield 78%. [$^2H_2$] = 99%.

Benzyl [$^2H_5$]benzoate. This was prepared by a standard procedure[31] from benzyl alcohol and [$^2H_5$]benzoyl chloride. Yield 76%. [$^2H_5$] = 98%.

[*O*-^{2}H]benzoin. This was prepared by three exchanges with MeOD at room temperature. [^{2}H] = 90%.

Compounds $PhCO_2CH_2C_6H_4R$. These were prepared by the following reported methods: R = 4-F,[32] 3-MeO,[33] 4-MeO,[34] 3-CN[32] and 4-CN.[32]

3-Fluorobenzyl benzoate. This was made by a standard method[32] from 3-fluorobenzyl alcohol and benzoyl chloride. Colourless liquid (bp 135–136 °C/0.5 mmHg). Yield 56%. Found, C, 73.04; H, 4.82. $C_{14}H_{11}O_2F$ requires C, 72.83; H, 4.65%. λ_{max}/nm (log ε, EtOH), 206, 230 (3.87, 3.90); ν_{max}/cm^{-1} 1720; δ_H(200 MHz) 5.35 (s, 2H), 7.20–8.11 (m, 9H); *m*/*z* 230 ($M^{\bullet+}$, 15%), 109 ($FC_6H_4CH_2^+$, 43), 105 ($PhCO^+$, 100), 77 (Ph^+, 22).

Compounds $RC_6H_4CO_2CH_2Ph$. These were prepared by the following reported methods: R = 4-F,[35] 3-MeO,[36] 4-MeO[37] and 4-CN.[38]

Benzyl 3-fluorobenzoate. This was made by a standard method[35] from 3-fluorobenzoyl chloride and benzyl alcohol. Colourless liquid (bp 122–123 °C/0.5 mmHg). Yield 84%. Found, C, 72.97; H, 4.66. $C_{14}H_{11}O_2F$ requires C, 72.83; H, 4.65%. λ_{max}/nm (log ε, EtOH), 206, 237 (3.88, 3.85); ν_{max}/cm^{-1} 1720; δ_H($CDCl_3$, 200 MHz), 5.37 (s, 2H), 7.2–7.9 (m, 9H); *m*/*z* 230 ($M^{\bullet+}$, 30%), 123 ($FC_6H_4CO^+$, 100), 95 ($FC_6H_4^+$, 36).

Benzyl 3-cyanobenzoate. This was made by a standard procedure[38] from 3-cyanobenzoyl chloride and benzyl alcohol. White crystals, mp 39–40 °C (from dichloromethane). Yield 82%. Found, C, 75.94; H, 4.67. $C_{15}H_{11}NO_2$ requires 75.64; H, 4.41%. λ_{max}/nm (log ε, EtOH), 210, 230 (4.23, 3.74); ν_{max}/cm^{-1} 2250, 1730; δ_H($CDCl_3$, 200 MHz), 5.40 (s, 2H), 7.4–8.4 (m, 9H); *m*/*z* 237 ($M^{\bullet+}$, 87%), 130 ($NC\text{-}C_6H_4CO^+$, 77), 102 ($NC\text{-}C_6H_4^+$, 34), 91 ($C_7H_7^+$, 100).

[$^2H_2$] Compounds RCO_2CD_2Ph (R = Me, Et, Pr^i and Bu^t. These compounds were made in 80–90% yield, by the standard reaction[39] from the appropriate acid chloride and [α,α-$^2H_2$]-benzyl alcohol. All products were distilled *in vacuo* and [$^2H_2$] = 99% in all cases. The purity of products was checked by ^{1}H NMR and positive ion MS.

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