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1,2 Anionic Rearrangements in the Gas Phase. The (Acyloxy)acetate–Acylhydroxyacetate and Related Rearrangements

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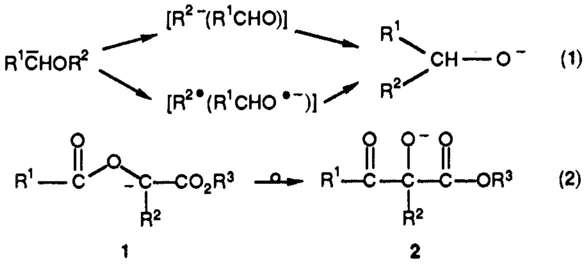
Abstract: The collisional activation mass spectra of deprotonated (acyloxy)acetates [$R^1CO_2C^-(R^2)CO_2R^3$] show a number of decompositions (e.g., losses of CO, C_2O_2, R^3OH, and HCO_2R^3) that occur following the 1,2 anionic rearrangment $R^1CO_2C^-(R^2)CO_2R^3 \xrightarrow{\circ} R^1COC(R^2)(O^-)CO_2R^3$. A similar gas-phase rearrangement is proposed for deprotonated α-acyloxyacetonitriles, i.e., $RCO_2C^-(H)CN \xrightarrow{\circ} RCOCH(O^-)CN$.

Introduction

Even electron anions upon collisional activation undergo a number of rearrangements in the gas phase: often these are analogous to condensed-phase reactions.[1] A number of 1,2 rearrangements have been reported recently,[2-5] of these the most studied is the Wittig rearrangement (eq 1, Scheme I, R^1 = Ph, $CH_2{=}CH$–; R^2 = alkyl or aryl).[2,6] The (acyloxy)acetate/acylhydroxyacetate rearrangement (eq 2, Scheme I, $R^1 = R^3$ = allyl; R^2 = H) has been reported to occur under basic conditions in the condensed phase.[7,8] Both this and the Wittig rearrangment formally involve 1,2 migration. It is suggested that in solution the (acyloxy)acetate/acylhydroxyacetate reaction is an anionic rearrangement proceeding through a hydroxy oxirane intermediate.[7b,c] Should rearrangement **1** → **2** occur in the gas phase, then **2** should be readily identifiable by its collision-induced decomposition pattern. This paper describes the complex rearrangements of deprotonated (acyloxy)acetates and of a cognate system.

Scheme I



Experimental Section

Collisional activation mass spectra (MS/MS) were determined with a VG ZAB 2HF instrument. Full experimental details have been reported previously.[9] Specific details were as follows: A chemical ionization slit was used in the ion source, the ionizing energy was 70 eV, the ion source temperature was 150 °C, and the accelerating voltage was 7 kV. Samples were introduced through the septum inlet (maintained at 100 °C) (source pressure 5×10^{-7} Torr). Deprotonation was effected by using NH_2^- (from NH_3; source pressure 1×10^{-5} Torr). The estimated source pressure was 10^{-1} Torr. Helium was used in the second collision cell (measured pressure 2×10^{-7} Torr), giving a 10% reduction in the main beam. An electric sector scan was used. Consecutive collision-induced and charge-reversal[10] mass spectra (MS/MS/MS) were measured with a Kratos MS 50 TA instrument. Operating details have been reported previously.[11] Substrates were deprotonated by MeO^- (from MeONO)[12] in a Kratos Mark IV chemical ionization source: source temperature 100 °C, electron energy 280 eV, emission current 500 μA, and accelerating voltage 8 kV. The substrate pressure was 2×10^{-5} Torr, and the methyl nitrite pressure was 1×10^{-6} Torr: estimated source pressure 10^{-1} Torr. The indicated pressure of helium in each of the two collision cells was 2×10^{-6} Torr, giving a 30% reduction in the main beam.

The following (acyloxy)acetates were made by reported procedures: (a) $MeCO_2CH_2CO_2Me$;[13] and (b) ($R^1CO_2CH_2CO_2Et$) (R^1 = Me, Et, *i*Pr, Bu, *i*Bu, *s*Bu, *t*Bu, C_5H_{11}, and Ph.[14] The following compounds are known: [$R^1CO_2CH(R^2)CO_2Me$] ($R^1 = R^2$ = Me;[15] R^1 = Me, R^2 = Et;[15] R^1 = Me, R^2 = *i*Pr;[16] R^1 = *t*Bu, R^2 = Me);[17] they were all prepared (in 65–90% yield) by acetylation[18] of the appropriate methyl α-hydroxycarboxylate.[19]

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(6) We generally represent the intermediate in gas-phase reactions (for convenience) as an ion/neutral complex. A radical/radical anion complex is possible if the electron affinity of $R^{•2}$ is sufficiently negative and that of R^1CHO is appreciably positive. It seems likely that such an intermediate is formed for condensed-phase Wittig rearrangements, since migratory aptitudes of groups are in the order of radical stabilities (Lansbury, P. T.; Pattison, V. A.; Sidler, J. D.; Bierber, J. B. *J. Am. Chem. Soc.* **1966**, *88*, 78. Schaefer, H.; Schöllkopf, U.; Walter, D. *Tetrahedron Lett.* **1968**, 2809. Schöllkopf, U. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 763.

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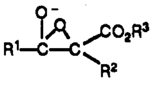

possible that *I* could dissociate to an acyl radical and a radical anion and that these species could recombine during the reaction sequence. We are not aware of any definitive work which might resolve this issue: such a possibility therefore cannot be excluded on the available evidence.

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Table I. Collisional Activation Mass Spectra of $[R^1CO_2CH(R^2)CO_2R^3 - H^+]^-$ and $[R^1COCR^2(OH)CO_2R^3 - H^+]^-$ Ions

	loss[b,c]								formation[b,c]			
neutral precursor[a]	H•	$(H_2,D^•)$	CO	C_2O_2	R^3OH	R^3OD	HCO_2R^3	DCO_2R^3	$R^1CO_2^-$	R^1CO^-	R^3O^-	R^{1-}
$MeCO_2CH_2CO_2Me$			42 (40.5)	1.5	100 (34)		54 (37)		2	1	1	
$Me^{13}CO_2CH_2CO_2Me$	see Figure 1											
$CD_3CO_2CH_2CO_2Me$[d]			100			79		77	2	1	1	
$MeCOCH(OH)CO_2Me$			43 (39.5)	2	100 (34)		46 (36.5)		2	1	1	
$MeCOCH(OSiMe_3)CO_2Me$[e]			44	2	100		47		2	1	1	
$MeCO_2CH_2CO_2Et$	6		58	2	100		52		1	1	1	
$MeCO_2CH_2CO_2C_2D_5$		4	52	4	94		100		1	1	1	
$EtCO_2CH_2CO_2Et$	7		71	14 (37)	91 (32.5)		100 (34)		1 (32)	1		
$EtCOCH(OH)CO_2Et$	18		85	10 (37)	86 (32.5)		100 (34)		1 (32.5)	1		
$i$$PrCO_2CH_2CO_2Et$	15	8	69	11	31		100		1	6	1	
$BuCO_2CH_2CO_2Et$	5		18	-	31		100		1	7	1	
$i$$BuCO_2CH_2CO_2Et$	8		50	6	87		100		1	9	1	
$s$$BuCO_2CH_2CO_2Et$	6		48	3	45		100		1	14	1	
$t$$BuCO_2CH_2CO_2Et$	2	10	100	64 (37)	30 (29.5)		49 (36)		4	11 (33.5)	2	
$t$$BuCO_2CH_2{}^{13}CO_2Et$	see Figure 2											
$t$$BuCOCH(OH)CO_2Et$			100	32 (37)	32 (30)		24 (36)		4	13 (34)	2	
$C_5H_{11}CO_2CH_2CO_2Et$	24	4	22	-	39		100			3		
$PhCO_2CH_2CO_2Et$			68 (76.5)	52 (51)	6 (37)		100 (38.5)		1	35 (38.5)	1	6 (38)
$PhCOCH(OH)CO_2Et$			42 (75.5)	44 (50)	5 (37.5)		100 (38.5)		2	36 (39)	2	7 (38.5)
$MeCO_2CH(Me)CO_2Me$	6		11 (50)	-	71 (38)		100 (34.5)		2			
$MeCOC(Me)(OH)CO_2Me$	8		10 (51)		68 (37.5)		100 (34)		2			
$MeCO_2CH(Et)CO_2Me$			5	-	84		100					
$MeCO_2CH(iPr)CO_2Me$	4		2.5	-	100		88					
$t$$BuCO_2CH(Me)CO_2Me$	8	12	2	-	12		100		2	1		

[a] Neutrals were deprotonated by NH_2^- to yield $(M-H^+)$ species [see (e) for an exception]. [b] Peaks are recorded as relative abundances with respect to the base peak (considered as 100%). [c] Values in parentheses are peak widths at half-height [volts; an average of five measurements (error ± 1 V)]. [d] Reaction of $CD_3CO_2CH_2CO_2Me$ with NH_2^- yields only an $(M-H^+)$ species. [e] $S_N2(Si)$ reaction (eq 6) forms $MeCOCH(O^-)CO_2Me$.

Table II. Mass Spectra (CA MS/MS/MS) of Selected Product Ions in the Mass Spectra (CA MS/MS) of $[R^1CO_2C^-(R^2)CO_2R^3]$

precursor ion (*m*/*z*)	product ion (*m*/*z*)	spectrum (CA MS/MS/MS) [*m*/*z* (loss) relative abundance]
$MeCO_2\bar{C}HCO_2Me$ (131)	-CO (103)	75 (CO) 100, 71 (MeOH) 32, 45 (58) 12, 43 (60) 6
	-MeOH (99)	71 (CO) 100, 57 (CH_2CO) 86, 55 (CO_2) 37, 43 (C_2O_2) 53, 41 (C_2H_2O), 29 (C_3H_2O) 12
	-HCO_2Me (71)[a]	70 (H•) 100, 45 (C_2H_2) 8, 43 (CO) 88, 41 (CH_2O) 37, 29 (CH_2CO) 2
$PhCO_2\bar{C}HCO_2Et$ (207)	-HCO_2Et (133)	105 (CO) 100, 77 (C_2O_2) 28
$t$$BuCO_2\bar{C}HCO_2Et$ (187)	-C_2O_2 (131)	101 (C_2H_6) 16, 87 (C_2H_4O) 53, 85 (C_2H_6O) 12, 45 (tBuCHO) 100

[a] The charge reversal (positive ion) MS/MS/MS data for *m*/*z* 71 is 56 (Me•) 14, 54 (HO•) 16, 53 (H_2O) 12, 42 (CHO•) 100, 29 (CH_2CO) 83, 27 (CO_2) 16, 26 (HCO_2•) 17, 15 (C_2O_2)7, 14 (C_2HO_2•)1.

All the acylhydroxyacetates are known, viz. $[R^1COC(OH)(R^2)CO_2R^3]$ ($R^1 = R^3 = Me$, $R^2 = H$;[20] $R^1 = R^3 = Et$, $R^2 = H$;[7] $R^1 = t$Bu, $R^2 = H$, $R^3 = Et$;[7] $R^1 = Ph$, $R^2 = H$, $R^3 = Et$;[7] and $R^1 = R^2 = R^3 = Me$).[20] The trimethylsilyl ether, $MeCOCH(OSiMe_3)CO_2Me$, was prepared by a standard procedure[21] from $MeCOCH(OH)CO_2Me$ and trimethylsilazide in 81% yield: bp 91–92 °C/17 mmHg; ^1H NMR (60 mHz in $CDCl_3$) δ 0.19 (9 H,s), 2.12 (3 H,s), 3.73 (3 H,s) and 5.65 (1 H,s). The compound is readily hydrolyzed and must be kept under a nitrogen atmosphere. $(M^{•+}-Me^•)^+$: found 189.057; $(C_7H_{13}O_4Si)^+$ requires 189.058.

Acyloxyacetonitriles used in this study were prepared by reported procedures, i.e., RCO_2CH_2CN (R = Me,[22] Et,[23] Pr,[23] and $PhCH_2$).[23]

Labeled Compounds. **(a)** $CD_3CO_2CH_2CO_2Me$ was prepared from methyl bromoacetate and sodium acetate-d_3 by the standard method[7] in 68% yield (d_3 = 99%).

(b) $Me^{13}CO_2CH_2CO_2Me$ was prepared from methyl bromoacetate and sodium acetate-*1*-^{13}C by the standard method[7] in 74% yield (^{13}C = 91%).

(c) $MeCO_2CH_2CO_2C_2D_5$ was prepared as above[7] by using ethyl-d_5 bromoacetate and sodium acetate in 63% yield (d_5 = 99%).

(d) $t$$BuCO_2CH_2{}^{13}CO_2Et$ was prepared from sodium pivalate[24] and ethyl bromoacetate-*1*-^{13}C by the standard method[7] in 57% yield (^{13}C = 91%).

(e) $CD_3CO_2CH_2CN$ was prepared from chloroacetonitrite and sodium acetate-d_3 by a standard procedure[22] in 84% yield (d_3 = 99%).

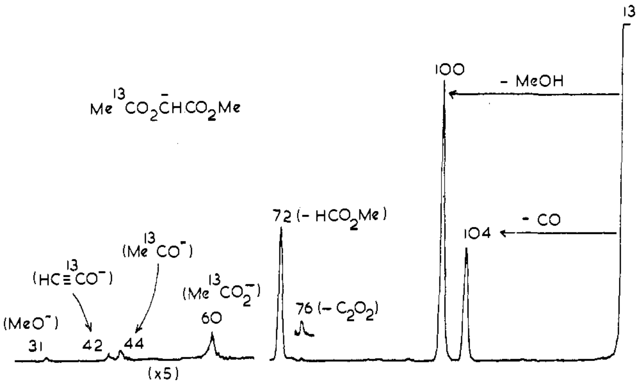

Figure 1. Collisional activation mass spectrum of $Me^{13}CO_2C^-(H)CO_2Me$ (VG ZAB 2HF spectrometer). For experimental details see Experimental Section. Decompositions occur both inside and outside the collision cell when a voltage of 1000 V is applied to the collision cell. A peak shifted from the normal value is produced by a collision process occurring in the cell, whereas an unshifted peak is due to processes occurring outside the cell. The unshifted peak is a combination of unimolecular and collision-induced processes (the latter due to leakage of gas from the cell). Results are [*m*/*z* (unshifted:shifted components)]: 104 (90:10), 100 (60:40), 72 (30:70), 60 (10:90), 44 (10:90), 42 (10:90), and 31 (70:30). *The presence of appreciable unshifted components for the rearrangement ions indicates that rearrangement 1–2 occurs in the ion source as well as on collisional activation.*

Results and Discussion

The (Acyloxy)acetate/Acylhydroxyacetate Rearrangement. The collision-induced mass spectra of a range of deprotonated (acyloxy)acetates together with those of the isomeric acyl-

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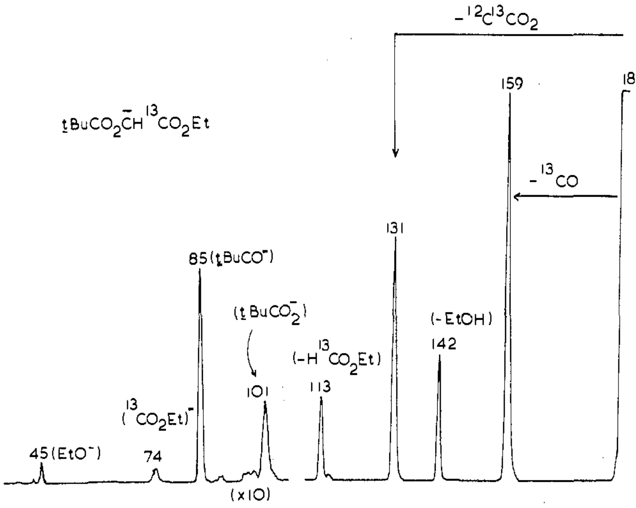
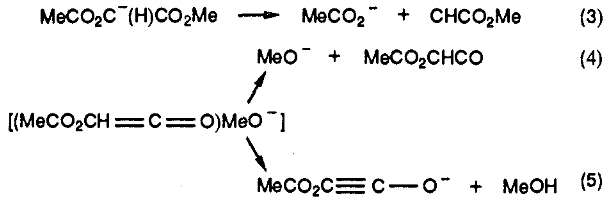


Figure 2. Collisional activation mass spectrum of tBuCO$_2$C$^-$(H)^{13}CO$_2$Et (VG ZAB 2HF spectrometer). A voltage of 1000 V applied to the cell gives the following results [m/z (unshifted:shifted components)]: 159 (90:10), 142 (60:40), 131 (90:10), 113 (50:50), 101 (10:90), 85 (10:90), 74 (50:50), and 45 (50:50).

hydroxyacetates are recorded in Table I. The spectra of two ^{13}C-labeled (acyloxy)acetates are illustrated in Figures 1 and 2. Data from MS/MS/MS experiments on certain product ions in the spectra of selected (acyloxy)acetates are collected in Table II.


$$MeCO_2C^-(H)CO_2Me \longrightarrow MeCO_2^- + CHCO_2Me \quad (3)$$
$$MeO^- + MeCO_2CHCO \quad (4)$$
$$[(MeCO_2CH{=}C{=}O)MeO^-]$$
$$MeCO_2C{\equiv}C{-}O^- + MeOH \quad (5)$$

An examination of the spectra of the simplest (acyloxy)acetate (Table I; Figure 1) sets the scene for this investigation. There are certainly rearrangement ions in the spectra, e.g., the losses of CO and C_2O_2. The latter process is of particular note: compare the abundances of the appropriate peaks in Figures 1 and 2. What is the origin of a process that can be so influenced by merely changing the nature of the alkyl substituent on the (acyloxy)-acetate? There are also other reactions that could conceivably originate from the unrearranged enolate anion, i.e., the formation of the acetate (eq 3) and methoxide (eq 4) ions and elimination of methanol (eq 5).[25] However, we will show subsequently that the latter two processes do not occur as shown in eqs 4 and 5.

The spectra of each of the five isomeric (acyloxy)acetate/acylhydroxyacetate pairs shown in Table I are qualitatively similar. The same peaks are present in the spectra of each isomeric pair (although the peak abundances are not always the same), and the widths (at half-height) of major peaks are the same (for selected isomeric pairs) within experimental error (see Table I). Thus, deprotonated (acyloxy)acetates and acylhydroxyacetates are, at least for the major rearrangement pathways, decomposing through common intermediates.[26]

$$MeCOCH(OSiMe_3)CO_2Me + NH_2^- \rightarrow MeCOCH(O^-)CO_2Me + Me_3SiNH_2 \quad (6)$$

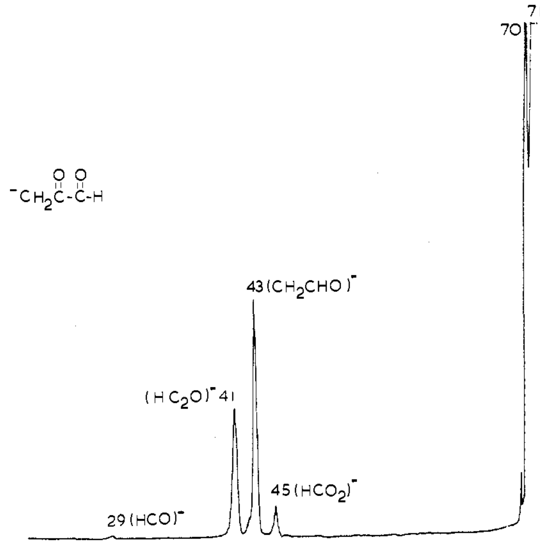
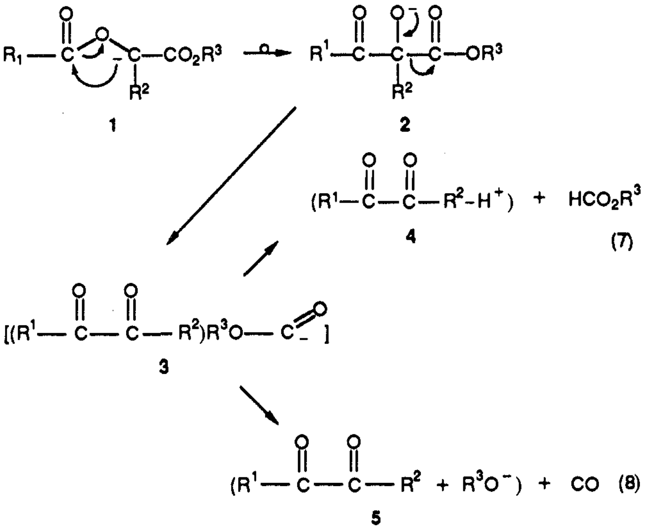


Figure 3. Collisional activation mass spectrum of $^-$CH$_2$COCHO (VG ZAB 2HF spectrometer). The charge reversal (positive ion) mass spectrum[9] of $^-$CH$_2$COCHO is as follows [m/z (loss) relative abundance]: 56 (Me$^\bullet$) 10, 54 (HO$^\bullet$) 15, 53 (H$_2$O) 15, 42 (CHO$^\bullet$) 100, 29 (CH$_2$CO) 76, 27 (CO$_2$) 12, 26 (HCO$_2^\bullet$) 14, 15 (C$_2$O$_2$) 4, 14 (C$_2$HO$_2^\bullet$) 1.

The data shown in Tables I and II suggest that the major fragmentations of (acyloxy)acetates may be rationalized by decomposition through the rearrangement ion **2** (Scheme I). This is shown particularly in two instances, i.e., the (almost) identical spectra of (i) MeCO$_2$C$^-$(Me)CO$_2$Me and MeCOC(Me)(O$^-$)-CO$_2$Me and (ii) MeCO$_2$C$^-$(H)CO$_2$Me, [MeCOCH(OH)CO$_2$Me − H$^+$], and authentic MeCOCH(O$^-$)CO$_2$Me [prepared by the S$_N$2(Si) reaction shown in eq 6].[27]

Scheme II



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(25) General rules for the fragmentation of even-electron organic anions have been reported—see ref 1.

(26) It is reported that certain cyclic acyloxy acetate/acyl hydroxyacetate isomers are interconvertible on heating.[8] Similar equilibria are not achieved for acyclic systems.[7] We have checked that such isomerization does not occur for the compounds under study here. For example, both MeCO$_2$CH$_2$CO$_2$Me and MeCOCH(OH)CO$_2$Me are stable on heating to 200 °C and can be distilled with no thermal rearrangement. The same is true for the isomeric pair MeCO$_2$CH(Me)CO$_2$Me and MeCOC(Me)(OH)CO$_2$Me.

(27) Deprotonation of an acyl hydroxyacetate should yield the enolate ion R^{1}COC(OH)CO2R^2 in preference to **2**. Although some **2** will be formed on deprotonation of an acyl hydroxyacetate, it is possible that the two species may be in equilibrium. Direct interconversion via 1,2 H$^-$ transfer seems unlikely since such processes have large barriers and are supposedly symmetry forbidden.[28] Perhaps interconversion occurs as

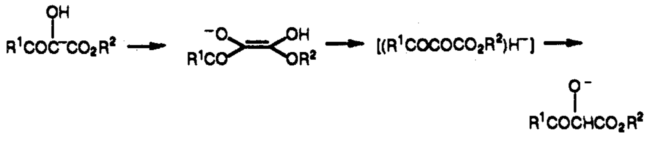
$$R^1COC^-(OH)CO_2R^2 \longrightarrow [(R^1COCOCO_2R^2)H^-] \longrightarrow R^1COCH(O^-)CO_2R^2$$

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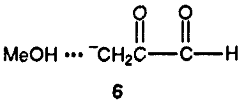
Table III. Collisional Activation Mass Spectra of (RCO_2CH_2CN - H^+) Ions and Labeled Analogues

RCO_2CH_2CN, R =	parent ion	loss											formation CN^-
		$H^•$	HCN	DCN	CH_2O	CHDO	CH_2CO	CD_2CO	MeCHCO	EtCHCO	PhCHCO	$HOCH_2CN$	
Me	M-H^+	1	16		82		100						22
CD_3	M-H^+			23		71		100					34
	M-D^+		10	12	63			100					20
Et	M-H^+		29		100				22				1
Pr	M-H^+		26		100					33			2
$PhCH_2$	M-H^+	20	13		18						5	100	0.5

Table IV. Collisional Activation and Charge Reversal (Positive Ion) Mass Spectra of Selected Product Ions in the Mass Spectrum of ($MeCO_2CH_2CN$ - H^+)

product ion (*m/z*)	spectrum (MS/MS/MS) [*m/z* (loss) abundance]
-HCN (71)	CA: 70 ($H^•$) 100, 45 (C_2H_2) 10, 43 (CO) 82, 41 (CH_2O) 36, 29 (CH_2CO) 2 CR: 56 ($Me^•$) 12, 54 ($HO^•$) 16, 53 (H_2O) 10, 42 ($CHO^•$) 100, 29 (CH_2CO) 89, 27 (CO_2) 14, 26 ($HCO_2^•$) 19, 15 (C_2O_2) 9, 14 ($C_2HO_2^•$) 12
-CH_2O (68)	CA: 41 (HCN) 5, 26 (CH_2CO) 100 CR: 54 (CH_2) 78, 52 (O) 86, 51 ($HO^•$) 62, 42 (CN) 100, 40 (H_2CN, CO) 84, 39 ($CHO^•$) 24, 38 (CH_2O) 16, 29 (C_2HN) 12, 26 (CH_2CO) 20, 14 (C_2NO) 12, 13 ($C_2HNO^•$) 2, 12 (C_2H_2NO) 1

Consider first the associated losses of carbon monoxide and alkyl formate, both of which originate from the acetate ester group (see Figures 1 and 2). The loss of alkyl formate is the major peak in the majority of spectra, whereas the loss of CO is a major fragmentation when R^2 = H but diminishes in importance when R^2 = alkyl. These processes are summarized in Scheme II. The alkoxycarbonyl ion in complex **3** can react as a base or an alkoxide anion donor,[29] thus, it competitively deprotonates the neutral (eq 7) and eliminates carbon monoxide (eq 8). The formation of product ion **4** is circumstantial evidence in favor of decomposition through **2**. In the particular case of $MeCO_2C^-(H)CO_2Me$, the loss of HCO_2Me produces $^-CH_2COCHO$, the identity of which is confirmed by a comparison of the MS/MS/MS data for *m/z* 71 (Table II) with the spectra of authentic $^-CH_2COCHO$ (Figure 3).[30] The structure of the product ion **5** (Scheme II) is also of interest. In the simplest case [$MeCO_2C^-(H)CO_2Me$], it could correspond to **6**, **7**, or **8**. The MS/MS/MS data on this product ion (*m/z* 103, Table II) show loss of CO and MeOH together with formation of $MeCO^-$ and HCO_2^-. Any of the ions could lose MeOH, while **6** (and perhaps **8**) could form HCO_2^- (cf. ref 29), but **7** is the most likely to form $MeCO^-$ (eq 9) and undergo the Riveros reaction (eq 10).[31] The most likely scenario is that loss of CO yields a mixture of **6** and **7** in this case.[32]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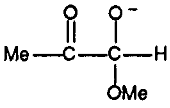
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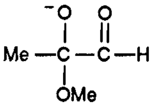
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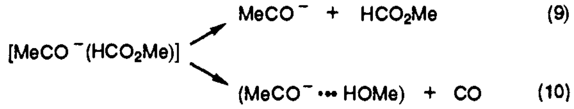
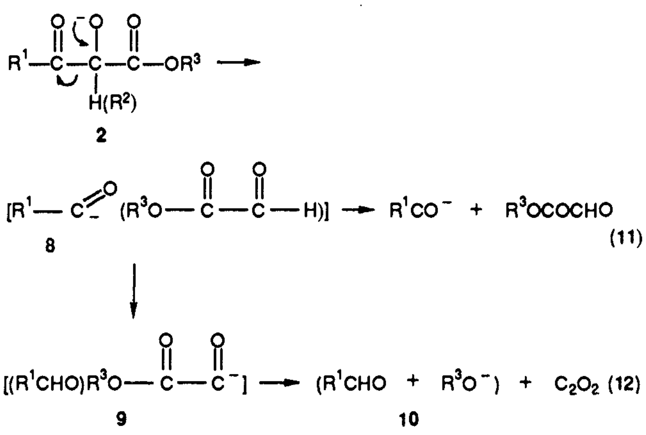


Scheme III



The most interesting process is loss of C_2O_2 since it is a fragmentation not observed before for negative ions. The process only occurs when R^2 = H and is most pronounced when R^1 = *t*Bu or Ph (Table I and cf. Figures 1 and 2). ^{13}C-Labeling (Figures 1 and 2) shows that the two adjacent acetate carbons are eliminated. This fragmentation is rationalized in Scheme III. Cleavage of **2** yields the acyl anion complex **8**. This complex may decompose directly (eq 11), or the acyl anion may deprotonate the neutral to yield complex **9**,[33] of which the anion, like its alkoxycarbonyl analogue (eq 8, Scheme I), is an alkoxide anion donor, forming **10**[34] and eliminating C_2O_2 (eq 12). This mechanism explains the experimental observations outlined above in that (i) if R^2 = alkyl, the specific deprotonation step **8** → **9** is not possible and (ii) if R^1 has an acidic proton, e.g., if **9** is say [(MeCHO) R^3O—C(=O)—C^-(=O)], proton transfer to [$^-CH_2CHO$ ($R^3OCOCHO$)] will compete with process **9** → **10**. Thus the reaction is favored when R^1 = *t*Bu or Ph.

Other decompositions involve the formation of $R^1CO_2^-$ and R^3O^- and the loss of R^3OH. The formation of $R^1CO_2^-$ is a minor process and may occur as shown in eq 3 since it occurs for both (acyloxy)acetates and acylhydroxyacetates.[35] This suggests that ion **2** may interconvert to **1** under conditions of collision activation. The loss of R^3OH is pronounced in all of the spectra listed in Table

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(29) Eichinger, P. C. H.; Bowie, J. H.; Hayes, R. N. *J. Chem. Soc., Perkin Trans. 2*, in press.

(30) This CA mass spectrum is most characteristic. Three of the fragmentations occur through ion complex [(CH_2CO) HCO^-], i.e., (i) direct dissociation to HCO^-, and (ii) the formyl anion acts as a H^- donor to yield $(CH_2CHO)^-$ and as a base to form HC_2O^-. In addition, a unique 1,2 anionic rearrangement occurs, viz.

(31) Blair, L. K.; Isolani, P. C.; Riveros, J. M. *J. Am. Chem. Soc.* **1973**, *95*, 1057. Faigle, J. F. G.; Isolani, P. C.; Riveros, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 2049. Rosenfeld, R. N.; Janinski, J. M.; Brauman, J. I. *J. Am. Chem. Soc.* **1979**, *101*, 3999. Sheldon, J. C.; Bowie, J. H. *Aust. J. Chem.* **1983**, *36*, 289.

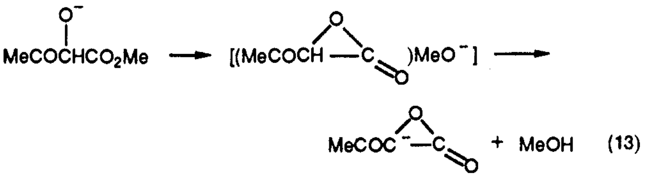
(32) (a) The formation of **8** seems unlikely since it should fragment through [($MeCO_2Me$) HCO^-] with elimination of CH_2O. This reaction is not observed. (b) A reviewer has indicated that identification of the product ion requires independent synthesis of **6**, **7**, and **8**. Unfortunately, we are unable to effect such syntheses; the fragmentation data nevertheless support the presence of **7**.

(33) Acyl anions are strong bases, e.g., ΔH°_{acid} CH_3CHO = 390 ± 2 kcal mol^{-1} (De Puy, C. H.; Bierbaum, V. M.; Damrauer, R.; Soderquist, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 3385).

(34) The structure of **10** could be [RO^- (R^1CHO)] or $R^1(R^2O)CHO^-$. In the case of $tBuCO_2\bar{C}HCO_2Et$, the collisional activation mass spectrum of the product ion (Table II) does not allow differentiation between the two possibilities.

(35) The widths of $EtCO_2^-$ peaks at half-height are the same (within experimental error) in the spectra of $EtCO_2CH_2CO_2Et$ and $EtCOCH(OH)$-CO_2Et (Table I).

I. Is it a fragmentation of **1** (eq 5), of **2**, or perhaps of both **1** and **2**? Abundance of peaks arising from losses of R^3OH are similar in the spectra of isomeric pairs shown in Table I. In addition, the widths at half-height are the same (within experimental error) for the appropriate peaks in the spectra of selected isomeric pairs (see Table I). Thus, it appears that loss of R^3OH from **1** and **2** involves a common decomposing intermediate; i.e., the process could be that shown in either eq 5 or eq 13. The MS/MS/MS data for the product ion formed by loss of MeOH from $MeCO_2C^-(H)CO_2Me$ are shown in Table II. The observed losses of CO, CH_2CO, and CO_2 are consistent with structure **11** of eq 13.[36] Thus, we propose that *all* major fragmentations in this series proceed after the rearrangement $R^1CO_2C^-(R^2)CO_2R^3$ $R^1COC(R^2)(O^-)CO_2R^3$. Data contained in the legend to Figure 1 indicate that some proportion of the rearrangement occurs in the ion source following deprotonation of the neutral.[37]



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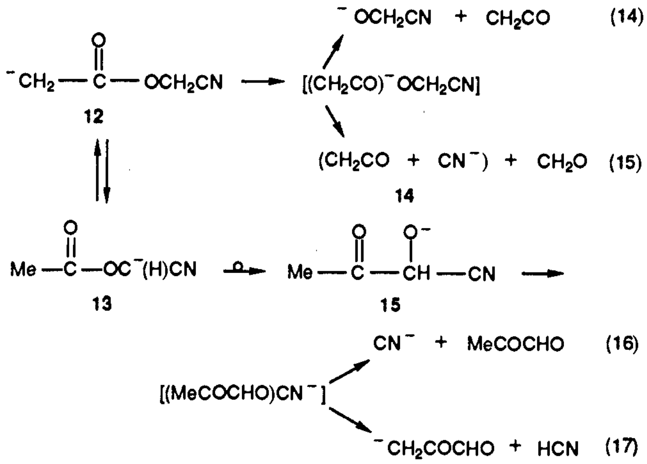
The α-(Acyloxy)acetonitrite/Acylcyanhydrin Rearrangement. The operation of the (acyloxy)acetate rearrangement has led us to investigate whether a similar reaction occurs for the analogous α-(acyloxy)acetonitrite system. The collision-induced mass spectra of several α-(acyloxy)acetonitrites are listed in Table III. Data from MS/MS/MS experiments on certain product ions in the spectrum of $(MeCO_2CH_2CN - H^+)$ are recorded in Table IV.

Reaction of $CD_3CO_2CH_2CN$ with NH_2^- forms both $^-CD_2CO_2CH_2CN$ and $CD_3CO_2C^-(H)CN$. The spectra of these two ions (Table III) indicate that they are able to equilibrate (by H^+ or D^+ transfer as appropriate) prior to decomposition. The decompositions of the two $(M-H^+)$ species of $MeCO_2CH_2CN$ are typical of all spectra recorded in Table III; they are summarized in Scheme IV. Ion **12** fragments through an ion complex to yield $^-OCH_2CN$ (eq 14):[38] ion $^-OCH_2CN$ is a CN^- donor in the ion complex, thus resulting in the elimination of formaldehyde (eq 15). MS/MS/MS data for product ion **14** are listed in Table IV and suggest the formation of $CH_2C(CN)O^-$.[39] Ion **12** fragments to form the product ions shown in eqs 16 and 17. The structure of the product ion of eq 17 is confirmed by comparison of its spectra (Table IV) with those of authentic $^-CH_2COCHO$ (Figure 3; cf. also Table II). These processes may occur by 1,2 rearrangement via **15** (by analogy with **1** → **2**).[40]

Scheme IV



In conclusion, this study confirms the operation of the facile gas-phase 1,2 anionic rearrangement $R^1CO_2C^-(R^2)CO_2R^3 \rightarrow R^1COC(R^2)(O^-)COR^3$, a reaction that occurs both in the ion source and upon collisional activation. An analogous gas-phase rearrangement may occur for the cognate α-(acyloxy)acetonitrite system, i.e. $RCO_2C^-(H)CN \rightarrow RCOCH(O^-)CN$. The latter reaction is not as facile as that observed for (acyloxy)acetates, since it competes unfavorably with 1,4 proton transfer (cf. **13** → **12**) in the case of (acyloxy)acetonitriles.[41]

Acknowledgment. This work was supported by the Australian Research Council and the Midwest Center for Mass Spectrometry, an NSF International facility.

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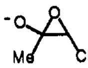
[36] Product ion $MeCO_2C\equiv CO^-$ (eq 5) should form $MeCO^-$, $MeCO_2^-$, and HC_2O^- and eliminate ketene. The first two ions are not observed.

[37] There is no evidence to indicate whether the oxirane ion shown in footnote 7b is an intermediate in the gas-phase rearrangement. Even if it is formed, it will certainly rearrange to $R^1COC(R^2)(O^-)CO_2R^3$.

[38] The ion $^-OCH_2CN$ is clearly not a strong enough gas-phase base to deprotonate CH_2CO (ΔH°_{acid} CH_2CO = 365 kcal mol^{-1}: Oakes, J. M.; Jones, M. E.; Bierbaum, V. M.; Ellison, G. B. *J. Phys. Chem.* **1983**, *87*, 4810) since no HC_2O^- is observed in this spectrum. In contrast, the base peak in the spectrum of $(PhCH_2CO_2CH_2CN - H^+)$ (Table III) is produced by the process $PhC^-(H)CO_2CH_2CN \rightarrow [(PhCHCO)^-OCH_2CN] \rightarrow PhC\equiv CO^- + HOCH_2CN$.

[39] The charge reversal spectrum of $(CH_2CO + CN^-)$ (Table IV, *m/z* 68) shows losses of CH_2, O, CN, and CH_2CO, reactions which are consistent with structure $CH_2C(CN)O^-$. Ion complex $[(CH_2CO)\ CN^-]$ should show only major losses of CH_2CO and CN. However, since peaks resulting from losses of CH_2CO and CN are observed, the presence of some $[(CH_2CO)\ CN^-]$ cannot be excluded on the available evidence.

[40] A reviewer has indicated that $[(MeCOCHO)CN^-]$ could be formed from **13** via the oxirane ion shown below. This possibility cannot be excluded



in this case because we have not been able to independently synthesize ion **15**.

[41] There are no major peaks in acyloxy acetate spectra which are associated with decomposition of a primary enolate ion. There is a very minor peak in the spectrum of $MeCO_2\overset{-}{C}HCO_2Me$ corresponding to HC_2O^- (Table I; cf. Figure 1). This must arise by the process $MeCO_2\overset{-}{C}HCO_2Me \rightarrow {}^-CH_2CO_2CH_2CO_2Me \rightarrow [(CH_2CO)^-OCH_2CO_2Me] \rightarrow HC_2O^- + HOCH_2CO_2Me$. Such peaks are not observed in other spectra. Thus, the 1,4 proton transfer, which is a major process for deprotonated acyloxyacetonitrites, is, at best, a very minor process for the corresponding deprotonated acyloxy acetates.