The Complex Anionic Rearrangements of Deprotonated α-Oximino Carbonyl Derivatives in the Gas Phase

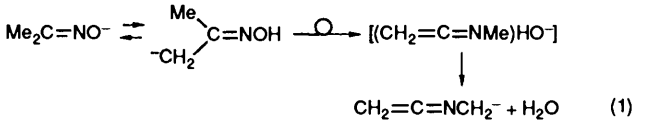
Gregory W. Adams,[a] John H. Bowie[a,*] and Roger N. Hayes[b]
[a] *Department of Organic Chemistry, The University of Adelaide, South Australia, 5001, Australia*
[b] *Department of Chemistry, University of Nebraska, Lincoln, Nebraska, 68588-0362, USA*

α-Oximino ketones $R^1COC(NOH)R^2$ deprotonate preferentially to form $R^1COC(NO^-)R^2$ and this anion decomposes by a variety of complex rearrangement processes. The two major fragmentations involve the following overall processes (i) and (ii).

(i) $R^1COC(NO^-)R^2 \xrightarrow{-O} R^1CO_2^- + R^2CN$, and
(ii) $R^1COC(NO^-)CH_2R \xrightarrow{-O} {}^-O(R^1)C{=}C{=}CH_2 + RNO$ (R = H or alkyl)

It is proposed that reaction (i) involves a four-centre reaction of O^- at the carbonyl carbon. No evidence of a Beckmann-type rearrangement is indicated for α-oximino ketones. The corresponding deprotonated α-oximino ketone *O*-methyl ethers also fragment by complex rearrangement. For example, MeCOC(NOMe)Me deprotonates to form two ions which are interconvertible on collisional activation. The enolate ion is the principal deprotonated species, and it decomposes by the overall process $^-CH_2COC(NOMe)Me \longrightarrow {}^-CH_2CN + CH_2CO + MeOH$. The other anion decomposes by loss of methanol. This is best rationalised either by the Beckmann process $MeCOC(NOMe)CH_2^- \longrightarrow [(CH_2{=}C{=}NCOMe)MeO^-] \longrightarrow CH_2{=}C{=}NCOCH_2^- + MeOH$, or a related Neber rearrangement. This investigation was aided by deuterium labelling, and product ion studies.

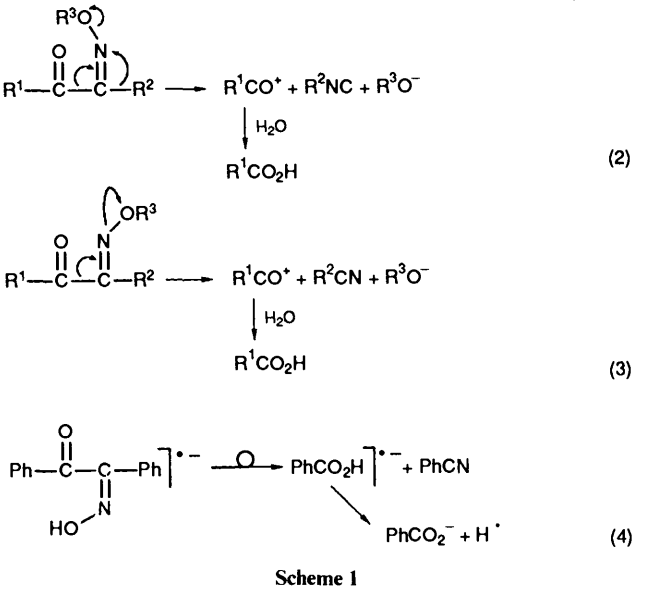
The classical Beckmann rearrangement[1] in the condensed phase is an acid-catalysed reaction: protonation at oxygen aids the reaction by elimination of H_2O, a good leaving group.[2] The group which migrates to N is often *trans* to hydroxyl, but isomerisation occurring prior to migration is also known.[3] Beckmann rearrangements for molecular radical cations seem not to have been reported, but such reactions do occur for protonated oximes in the gas phase.[4]



(1)

It has been proposed that collision induced loss of water from deprotonated oximes in the gas phase is best rationalised by a negative ion Beckmann rearrangement.[5] This 1,2 anionic rearrangement process is illustrated in eqn. (1): the alternative rearrangement which involves direct attack of the methylene anion at nitrogen (a Neber-type rearrangement)[6] is suggested to be a less likely possibility.[5]

Variations on the Beckmann rearrangement have been known for more than a hundred years. α-Oximino ketones are interesting illustrations. For example, for *syn* isomers in the condensed phase, it is proposed that, under acid or basic conditions, the reaction takes the course shown in eqn. (2), whereas the *anti* isomers react as shown in eqn. (3).[7,8] Group migration occurs in eqn. (2) but not in eqn. (3). In support of the latter sequence, the reaction of *anti* $PhCOC(NOH)CH_2Ph$ with benzene sulphonyl chloride and HO^- yields benzoic acid, phenylacetonitrile and $PhCOC(NOCOPh)CH_2Ph$.[8,†] The



Scheme 1

only report of the fragmentation of a corresponding negatively charged species in the gas phase is shown in eqn. (4): here, the molecular radical anion undergoes rearrangement to yield the benzoic acid molecular anion which decomposes to form the benzoate anion.[10]

This paper is concerned with the fragmentation behaviour of deprotonated α-oximino ketones and related systems. Do they exhibit rearrangement processes, and, if so, is there any correlation between the products produced in the gas and condensed phases?

Results and Discussion

α-Oximino ketones have a number of centres whose acidities should differ by only some 30 kJ mol^{-1}. For example, the gas

† A major fragmentation of ions $R^1COC(\overset{+}{N}OH_2)R^2$ in the gas phase is formation of R^1CO^+: for example the collisonal activation MS/MS data for $MeCOC(\overset{+}{N}OH_2)H$ (*m/z* 88) is [*m/z* (loss) relative abundance]: 87($H^•$)100, 70(H_2O)37, 46(CH_2CO)43, 43(HCN + H_2O)34 and 28(CH_2CO + H_2O)8.[9]

Table 1 Collisional activation mass spectra of $M - H^+$ ions derived from α-oximino ketones $R^1COC(NOH)R^2$ [numbers refer to relative abundances with respect to base peak (100%): values in brackets are peak widths at half height (volts ±2) (1 eV = 96.49 kJ mol^{-1})]

$R^1COC(NOH)R^2$		Loss															Formation								
R^1	R^2	H·	D·	Me·	CD_3·	Et·	Pr·	H_2O	HOD	HCN	DCN	HNO	DNO	MeNO	CD_3NO	EtNO	PrNO	R^1CO_2H	$R^1CO_2^-$ (–R^2CN)	R^1⁻	R^1CO^-	CNO^-	HC_2O^-	DC_2O^-	CN^-	DO^-	HO^-
Me	H	25		1				2		100[a]									100 (168)			18	28		2		
Me	Me	75		1				3		48		100		13				25	75 (228)			8	18		1		1
CD_3	Me	40	10		1[b]			2[b]	1		39 (180)	100			12			15	78 (225)			20[c]		20[c]	1		
Me	Et	90		6				3		27 (175)[d]		65		62				36	100			5	15		1		1
CD_3	Et	100	15	12				2	6		29[d]	84		25	26			12	68			18[b]		18[b]	1	1	
Me	CD_2Me	100	20	12				3	3	24[d]		32	28	54				12[e]	71			8	7		1		
Me	CH_2CD_3	100		3	15[b]			15[b]		25[d]		73		22	18			<10[f]	48			4	5		1		1
Me	Pr	45		9		100		2		<5[d,f]		51		9		48		<10[f]	28			5	8				
Me	Pr^i	20		5				2		16[d]		45		65				25	100			15	18		1		1
Me	Bu	33		2			34	2		5[d]		100		11			12	16	21			4	6		1		
Me	Bu^i	35					100					43		15			56	18	35			1	8		1		
Me	Bu^s	30		2		100[f]				100[f]		93		51		22		<10[f]	19			4	5		1		1
Me	COMe	100												25				11	24			10			2		
Me	Ph	100		2				9		3		2		100				18	14 (215)			3	6		1		
CD_3	Ph	100							6		2	2			72			18	14			6[b]		6[b]			
Et	Me	65				9						100				29		6	58 (210)			3			1		
Pr	H	100					6			52[a]		4					5		52 (174)			2					
Pr^i	H	85					6			100[a]							8		100 (175)			3					
Pr	Et	60		5								46		12			29	8	100 (197)			2					
Bu	Pr	51				75						100				48	26	6	98								
Bu^t	H	26										43							100								
Ph	H	100						21		100[a]									100 (160)	22		2			1		
Ph	Me	100						20				28							33 (177.5)	10	18	1					
C_6D_5	Me		100						11			66							65 (175)	15	9	1					
Ph	Ph	100						32				2							18 (160)	5							
C_6D_5	Ph	100	<20[e]						45				3						15	2							
$C_6H_2D_3$	Ph	100	<30[e]						30				2						16	2							

[a] Loss of HCN gives $R^1CO_2^-$ in these cases. [b] CD_3 and H_2O = 18 a.m.u. [c] CNO^- and DC_2O^- = 42 a.m.u. [d] Composite peak–minor gaussian component superimposed on dish-shaped peak. [e] Loss of R^1CO_2D in this case. [f] Not fully resolved.

Table 2 Fragmentation data for product ions in the mass spectra of deprotonated α-oximino ketones

Precursor ion (*m/z*)	Product ion (*m/z*)	Spectrum type	Spectrum [*m/z* (abundance)]
$[MeCOC(NOH)Me - H]^-$ (100)	100 – MeCN (59)	CA MS/MS/MS[a]	58 (100), 41 (18), 15 (30)
		CR[b] MS/MS/MS	45 (25), 44 (100), 43 (30), 42 (42), 41 (15), 29 (26), 28 (24), 15 (20), 14 (15)
	100 – HNO (69)	CA MS/MS/MS	67 (18), 54 (100), 41 (27)
		CR[b] MS/MS/MS	54 (20), 53 (42), 51 (21), 50 (14), 43 (100), 39 (18), 27 (22), 26 (25), 15 (19)
	100 – HCN (73)	CA MS/MS[c]	72 (100), 71 (20), 58 (8), 55 (20), 44 (5), 27 (1), 17 (0.2)
		CR[b] MS/MS[c]	57 (2), 56 (2), 55 (2), 53 (2), 45 (24), 44 (100), 42 (20), 29 (50), 28 (48), 27 (63), 26 (35), 17 (1), 16 (1), 15 (1), 14 (1)
$EtCO_2$ (73)		CA MS/MS	72 (100), 71 (22), 58 (8), 55 (28), 44 (7), 27 (1), 17 (0.3)
		CR[b] MS/MS	57 (2), 56 (2), 55 (2), 53 (2), 53 (2), 45 (28), 44 (100), 42 (22), 29 (48), 28 (47), 27 (59), 26 (32), 17 (1), 16 (1), 15 (1), 14 (1)
$[MeCOC(NOH)Et - H]^-$ (114)	114 – HCN (87)	CA MS/MS[c,d]	86 (100), 85 (6), 71 (31), 69 (16), 58 (56), 44 (4), 41 (3), 27 (1)
		CR[b] MS/MS[c,d]	86 (1), 71 (2), 60 (3), 55 (9), 53 (3), 45 (26), 44 (100), 43 (58), 41 (87), 39 (94), 29 (24), 28 (31), 27 (46), 26 (26)
$PrCO_2^-$ (87)		CA MS/MS	86 (100), 85 (9), 71 (29), 69 (15), 58 (48), 44 (5), 41 (4), 27 (1)
		CR[b] MS/MS	86 (1), 71 (3), 60 (3), 55 (11), 53 (3), 45 (31), 44 (100), 43 (62), 41 (91), 39 (96), 29 (20), 28 (28), 27 (48) 26 (22)
$[MeCOC(NOH)Ph - H]^-$ (162)	162 – PhCN (59)	CA MS/MS[c]	58 (100), 41 (14), 15 (28)
$[PhCOC(NOH)Ph - H]^-$ (224)	224 – H_2O (206)	CA MS/MS[c]	205 (100), 177 (10), 154 (0.5), 130 (1), 102 (2), 90 (1)
	224 – PhCN (121)	CA MS/MS[c]	120 (100), 77 (96), 76 (18)
$PhCO_2^-$ (121)		CA MS/MS	120 (100), 77 (94), 76 (17)
$[C_6D_5COC(NOH)Ph - H]^-$ (229)	229 – HOD (210)	CA MS/MS[c]	209, 208[e] (100), 181 (1), 180 (5), 134 (0.5), 102 (1), 90 (1)
	229 – PhCN (126)	CA MS/MS[c]	124 (46), 82 (100), 82 (8)

[a] Weak spectrum. *m/z* 44 is not detected because of baseline noise. For CA and CR mass spectra of $MeCO_2^-$ and $^-(CH_2CO_2H)$ see ref. 15. [b] Charge reversal positive ion spectrum. The negative ion is converted into a decomposition positive ion by charge stripping in the collision cell.[16] [c] The MS/MS/MS data are lost in baseline noise. The spectra recorded are those of the appropriate species formed by dissociation of the $(M - H)^-$ species in the ion source. [d] This is the spectrum of the propionate anion (see below). It is quite different from that of the possible isomer $^-CH_2CO_2Me$; *cf.* ref. 17. [e] Not resolved.

phase ΔH°_{acid} values for $Me_2C{=}NOH$,[11] $(CH_3)_2C{=}NOMe$,[12] and CH_3COR[13] are 1531, 1561 and *ca.* 1544 kJ mol^{-1} respectively. This has two consequences: (*i*) deprotonation (by NH_2^-) should be effected preferentially at the –NOH position, but some deprotonation could also occur at other centres, *e.g.* on both methyl groups of MeCOC(NOH)Me, and (*ii*) proton transfer may occur between all three acidic centres under conditions of collisional activation.[5]

The following experiments are in qualitative accord with the predictions of relative acidities: (*i*) when MeCOC(NOH)Me is introduced into the heated septum inlet system together with D_2O (using a method developed by Shannon),[14] one H is totally exchanged within 5 s of the injection of D_2O, while three other hydrogens are partially exchanged within 3 min [this is demonstrated by monitoring the $M^{+\cdot}$ region] (*ii*) reaction of $CD_3COC(NOH)Me$ with NH_2^- yields at least 80% of an $(M - H)^-$ species (a more precise estimate cannot be given—the problem is that the precursor cannot be specifically trideuteriated, *i.e.* $D_3 - 90$, $D_2 - 10\%$) and (*iii*) the spectra of $[CD_3COC(NOH)Me - H]^-$ and $[CD_3COC(NOD)Me - D]^-$ (each spectrum measured within 30 s of injection of D_2O) are identical within experimental error.

The Rearrangement Reactions of Deprotonated α-Oximino Ketones.—Spectra are listed in Table 1 and Figs. 1–3. The mass spectra of certain product ions from selected spectra are recorded in Table 2. All of the collisional activation spectra are dominated by rearrangement ions. In the general case of $[R^1COC(NOH)CH_2R - H]^-$, processes are noted which result in (*i*) the formation of $R^1CO_2^-$ and the loss of R^1CO_2H, (*ii*) the loss of both 'R^1NO' and 'RNO' (R = H or alkyl), (*iii*) the loss of HCN when R^1 = Me and R = H or Me, and (*iv*) the loss of H_2O, particularly when R^1 = Ph.

(*a*) *The formation of* $R^1CO_2^-$ *and the loss of* R^1CO_2H. The carboxylate ion $R^1CO_2^-$ is a major component of all spectra (Table 1) and the resultant peak is always very broad and dish-shaped (see Figs. 1–3: also Table 1). Let us consider a simple case, $[MeCOC(NOH)Me - H]^-$. The peak width of the rearrangement peak is 228 ± 2 V,* the widest peak yet recorded for a negative ion dissociation. Broad peaks are often associated with reactions having tight transition states and appreciable reverse activation energies.[18] The data collected in Table 2 confirm the product ion to be the acetate ion $MeCO_2^-$, and not the acetic acid enolate $^-(CH_2CO_2H)$.[15]† Five mechanisms need to be considered for the formation of $MeCO_2^-$ and the associated elimination of $MeCO_2H$; these are summarised in Scheme 2. The first two possibilities are the Beckmann- and Neber-type rearrangements shown in eqn. (5). Here, proton transfer **1** ⟶ **2** (some of **2** may also be formed during the initial ionization), precedes either process, and the final ion molecule complex $[^-CH_2CN(MeCO_2H)]$ may decompose to both $MeCO_2^-$ and $^-CH_2CN$. In these cases, if the reaction is thermodynamically controlled, the predominant process would be formation of $MeCO_2^-$ since $^-CH_2CN$ is a stronger base than $MeCO_2^-$ (ΔH°_{acid} $MeCO_2H$ and CH_3CN are 1435[13] and 1560[11] kJ mol^{-1} respectively). The third possibility is shown in eqn. (6): here, cyclisation in **1** produces an ion–molecule complex which should fragment to $MeCO_2^-$ (the alternative formation of $^-CH_2CN$ would require the complex to have an excess energy of some 100 kJ mol^{-1}, see above). The fourth and fifth scenarios are shown in eqn. (7). Cyclisation in **3** to form **4**, followed by nucleophilic displacement could yield ion–molecule complex **6**. Alternatively, complex **6** could be formed following

* 22 000 ± 193 kJ mol^{-1}; 1 eV = 96.49 kJ mol^{-1}.

† The data in Table 2 show the product ion to be $PhCO_2^-$ when R^1 = Ph.

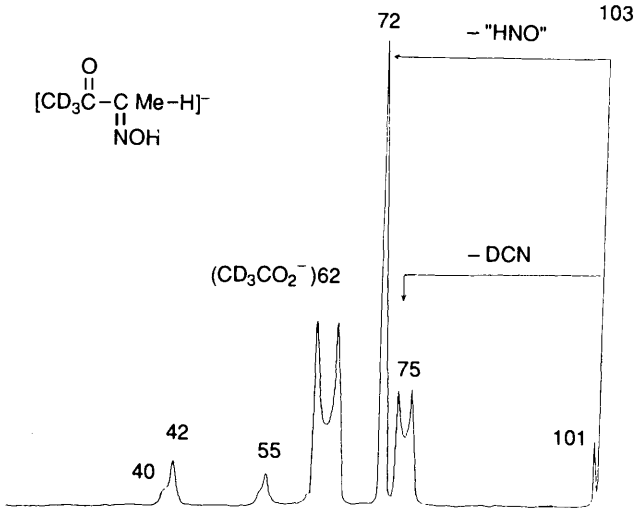


Fig. 1 CA Mass spectrum of $[CD_3COC(NOH)Me - H]^-$. VG ZAB 2HF instrument. For experimental details see Experimental section. Decompositions occur both inside and outside the collision cell when a voltage of 1000 V is applied to the collision cell. A peak shifted from the normal value indicates a process occurring by collision in the cell. The unshifted peak is due to processes occurring outside the cell: a combination of unimolecular and collision induced reactions (the latter due to leakage of gas from the cell). Results are [*m/z* (unshifted:shifted components)]: 74 (50:50), 72 (20:80), 62 (60:40), 55 (50:50), 42 (40:60). Thus rearrangements occur by both unimolecular and collision induced processes.

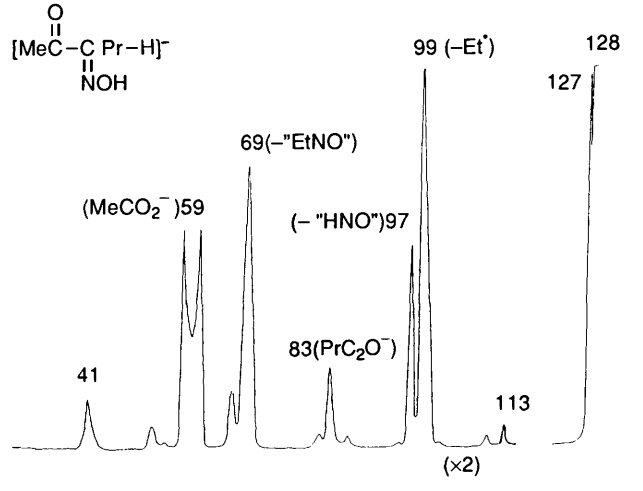


Fig. 2 CA Mass spectrum of $[MeCOC(NOH)Pr - H]^-$. VG ZAB 2HF instrument.

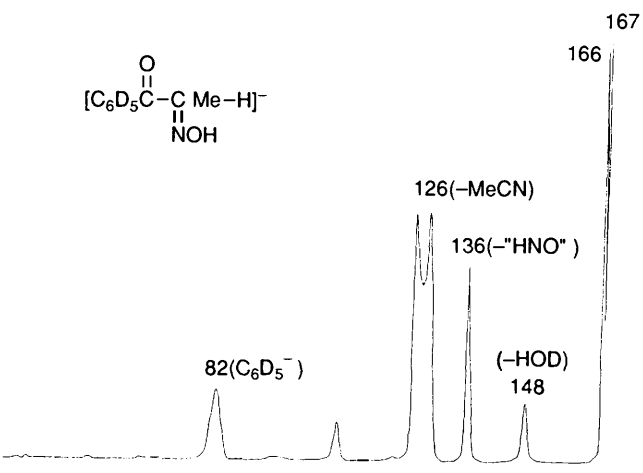
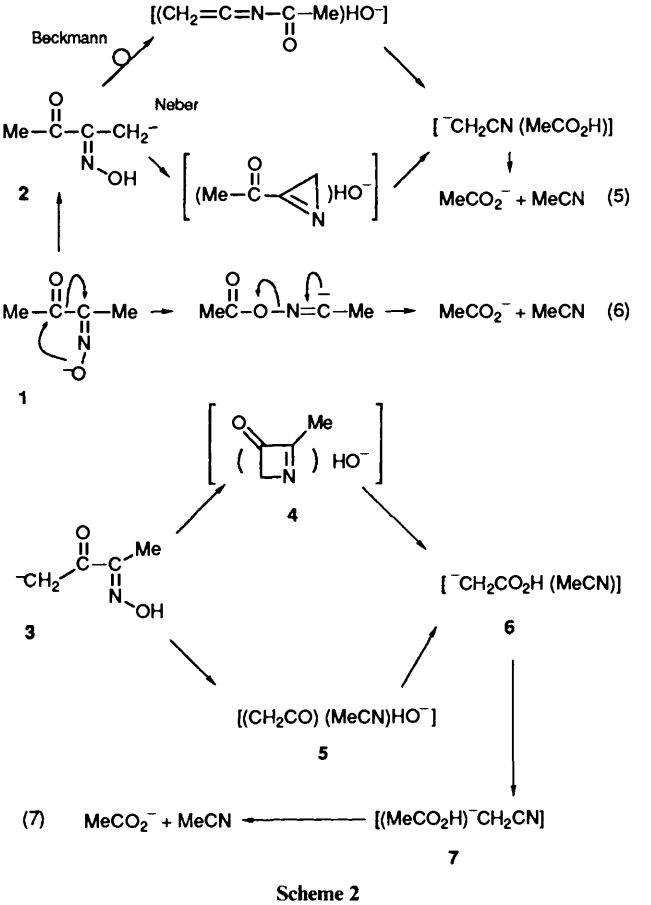


Fig. 3 CA Mass spectrum of $[PhCOC(NOH)Me - H]^-$. VG ZAB 2HF instrument. When a voltage of 1000 V is applied to the collision cell the following results are obtained [*m/z* (unshifted:shifted components)]: 148 (30:70), 136 (15:85), 126 (75:25), 108 (10:90), 82(20:80).



Scheme 2

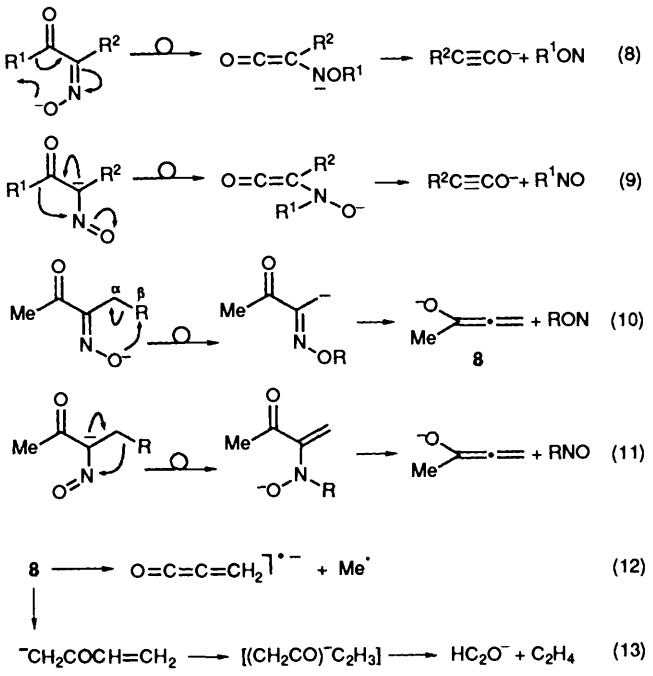
cleavage to **5**. The acetic acid enolate ion of **6** could deprotonate acetonitrile to form **7** if the ion complex has excess energy [ΔH°_{acid} CH_3CO_2H and CH_3CN are 1527[15] and 1560[11] kJ mol^{-1}] and **7** would then decompose to products.

Consider now the case of $[CD_3COC(NOH)Me - H]^-$. The reactions corresponding to those shown in eqns. (5) and (6) should produce $CD_3CO_2^-$; the corresponding product from eqn. (7) should be $CD_2HCO_2^-$. Experimentally, the symmetrical product peak shown in Fig. 1 is centred precisely at *m/z* 62, thus the product ion is exclusively $CD_3CO_2^-$. Therefore the mechanism is either the Beckmann/Neber process [eqn. (5)] or the O^- cyclisation [eqn. (6)].

All spectra listed in Table 1 show $R^1CO_2^-$ peaks: all are dish-shaped and very wide. There must, therefore, be a high probability that all $R^1CO_2^-$ ions are formed by the same overall mechanism. Yet $R^1CO_2^-$ ions are formed in systems where R^2 = H, COMe, and Ph, *i.e.* where neither the Beckmann nor the Neber rearrangement [*cf.* eqn. (5)] can occur. Circumstantial evidence thus favours $R^1CO_2^-$ formation (and R^1CO_2H loss) by the four centre reaction shown in eqn. (6).

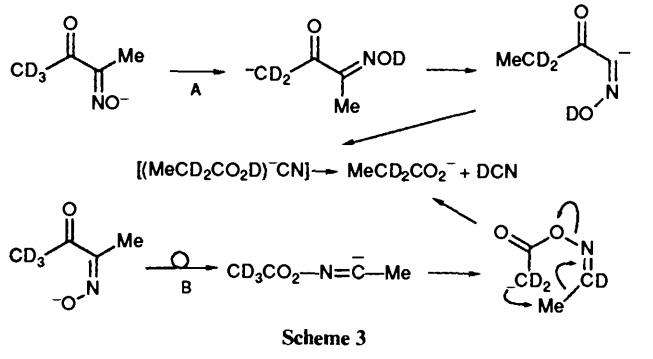
(*b*) *Other fragmentations of deprotonated α-oximino ketones.* There are two types of rearrangement resulting in losses of 'RNO'; both involve migration of a group to either N or O. The first is represented by the general processes shown in eqns. (8) and (9) in which R^1 migrates respectively to oxygen or nitrogen. We cannot distinguish between the two processes. This process occurs in the majority of spectra, *e.g.* see the losses of 'CD_3NO' (Fig. 1) and 'MeNO' (Fig. 2) to yield *m/z* 55 and 83 respectively.

The second rearrangement is best introduced by dealing first with the loss of 'HNO'. This loss is pronounced whenever the



carbon adjacent to the oxime function bears at least one hydrogen. In Fig. 1, the loss of 'HNO' gives the base peak of the spectrum: the process may occur as shown in eqn. (10), [migration to O, R = H], or eqn. (11) [migration to N, R = H]. Both processes yield product **8**.*† The fragmentation data of this product ion are listed in Table 2, and are consistent with structure **8**. For example, the major collision induced dissociations are rationalised in eqns. (12) and (13), while the corresponding charge reversal spectrum exhibits major loss of methane and formation of $MeCO^+$.

When $R^2 \geqslant Et$, competitive cyclisations involving the various β substituents [see eqn. (9)] may result in the losses of both 'HNO' and 'RNO' (R = alkyl). For example (*i*) $MeCOC(NO^-)Pr$ shows losses of 'HNO' and 'EtNO' [to *m/z* 97 and 69 respectively (Fig. 2)], while the isomer $MeCOC(NO^-)Pr^i$ (Table 1) loses 'HNO' and 'MeNO', and (*ii*) $MeCOC(NO^-)Bu^s$ loses 'HNO', 'MeNO' and 'EtNO'.

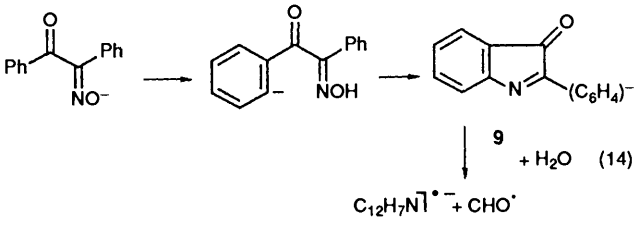


Scheme 3

* The process involving RNO loss is favoured thermodynamically: however it is possible that the alternative process involving loss of RON is kinetically favoured.

† The loss of 'HNO' from $MeCOC(NO^-)Et$ is quite unusual. The data in Table 1 show that while $CD_3COC(NO^-)Et$ and $MeCOC(NO^-)CH_2CD_3$ both lose 'HNO' specifically, $MeCOC(NO^-)CD_2Me$ loses 'HNO' and 'DNO' in almost equal amounts. Thus, in this case, process (9) (R = D) has a pronounced deuterium isotope effect. This effect induces the competitive transfer of a proton from the terminal methyl group, a process not observed for the other labelled analogues. Similar behaviour has been noted before for deuterium labelled ketones.[19]

Losses of HCN are noted for the majority of spectra listed in Table 1. The loss is most pronounced when R^2 = H; in these cases loss of HCN yields $R^1CO_2^-$ [eqn. (6)]. However, loss of HCN also occurs when R^2 = alkyl: the process becomes less pronounced with elaboration of R^2 (Table 1). The reaction is illustrated in Fig. 1, where the loss of DCN produces a dish-shaped peak centred at *m/z* 75. The corresponding peak in the spectrum of the unlabelled compound is identified as the propionate anion by the data listed in Table 2. This is a most unusual rearrangement: two possible reaction sequences are outlined in Scheme 3 and we cannot distinguish between them. The first, route A, involves an alkyl migration through a four centre state; the second, route B, follows the initial reaction shown in eqn. (6), but then D^+ transfer and alkyl migration through a six-centre state yields the required products. Interestingly, when R^2 = Et, the peak resulting from loss of HCN is composite, with a narrow central gaussian peak superimposed on the dish-shaped peak. The product ion is the butyrate anion (see Table 2), so it seems likely in this case that routes A and B are both operating.



Losses of H_2O are major reactions when R^1 = Ph (see *e.g.* Fig. 3). The process is most pronounced when R^1 = R^2 = Ph; labelling studies (Table 1) show that the loss involves a hydrogen atom from each ring. This suggests proton transfer to O^- followed by cyclisation [eqn. (14)] to form **9**. The fragmentation data of this product ion (Table 2) are consistent with such a structure, since the characteristic fragmentation of $[PhCOC(NO^-)Ph - H_2O]$ is loss of CHO•, whereas $[C_6D_5COC(NO^-)Ph - HOD]$ loses mainly CDO•. Losses of CHO• have been observed before for cyclic systems containing CO functionality.[20]

$$CH_3COC(NO^-)CH_2R \longrightarrow CH_3COC(NO^-)\dot{C}HR + H^\bullet \quad (15)$$

$$R^1COC(NO^-)CH_2\ alkyl \longrightarrow R^1COC(NO^-)CH_2^\bullet + alkyl^\bullet \quad (16)$$

$$^-CH_2COC(NOH)R^2 \longrightarrow [(CH_2CO)\ ^-C(NOH)R^2] \longrightarrow HC_2O^- + R^2CHNOH \quad (17)$$

Other major reactions observed in the spectra are standard and have been noted in cognate systems, *e.g.* the loss of H• [for the major loss see eqn. (15)],[5,21] the loss of an alkyl radical [or (alkyl − H•) + H•] [eqn. (16) see also Fig. 2],[20] the formation of HC_2O^- [eqn. (17)], and the formation of CNO^-.[5]

The Rearrangement Reactions of Deprotonated α-Oximino Ketone O-Methyl Ethers.—We have proposed that the complex rearrangements of deprotonated α-oximino ethers proceed through the NO centre [eqns. (6), (8)–(11) and Scheme 3]. What will happen if the NO position is 'blocked', as in $R^1COC(NOMe)R^2$? Depending on the nature of R^1 and R^2, deprotonation can only occur at these centres, and the subsequent fragmentations must differ substantially from those described above.

The collisional activation mass spectra of deprotonated ethers $R^1COC(NOR^3)R^2$ are listed in Table 3. The spectra are,

Table 3 Collisional activation mass spectra of $(M - H^-)$ and $(M - D^-)$ ions from $R^1COC(NOR^3)R^2$

$R^1COC(NOR^3)R^2$			Parent ion	Loss														Formation					
R^1	R^2	R^3		H•	D•	Me•	CD_3•	Et	MeOH	MeOD	CD_3OH	'MeON'	'CD$_3$ON'	$C_3H_6O_2$	$C_3H_4D_2O_2$	$C_3H_3D_3O_2$	$C_8H_8O_2$	$R^2C_2O^-$	HC_2O^-	DC_2O^-	MeO^-	CD_3O^-
Me	H	Me	$(M - H)^-$	72		18			34					100				20			29	
Me	Me	Me	$(M - H)^-$	42		45			76			18		100					<5[a]		5	
Me	Me	CD_3	$(M - H)^-$	49			34				58		12			100			<5[a]			6
CD_3	Me	Me	$(M - D)^-$[b]	48	9	39			29	40		12			100					6	6	
CD_3	Me	Me	$(M - H)^-$[b]			57				100		19			33	40				8	5	
Me	Et	Me	$(M - H)^-$	75		15			32			3		100					<5[a]		1	
Me	Pr	Me	$(M - H)^-$	100		3		8[c]	15			2		72				3	<5[a]		1	
Me	Pr	CD_3	$(M - H)^-$	100			2	4[c]			19		2			67			<5[a]			2
Me	Ph	Me	$(M - H)^-$	5					6					100							2	
Ph	H	Me	$(M - H)^-$	86		6			100								<1					
Ph	D	Me	$(M - D)^-$	100		7			70								<1					

[a] Unresolved. [b] $(M - D)^-$:$(M - H)^-$ = 3:1. [c] This is a standard reaction:[5] $^-CH_2COC(NOMe)Pr \longrightarrow {}^-CH_2COC(NOMe)CH_2^{\bullet} + Et^{\bullet}$ [*cf.* eqn. (16); see also Fig. 2].

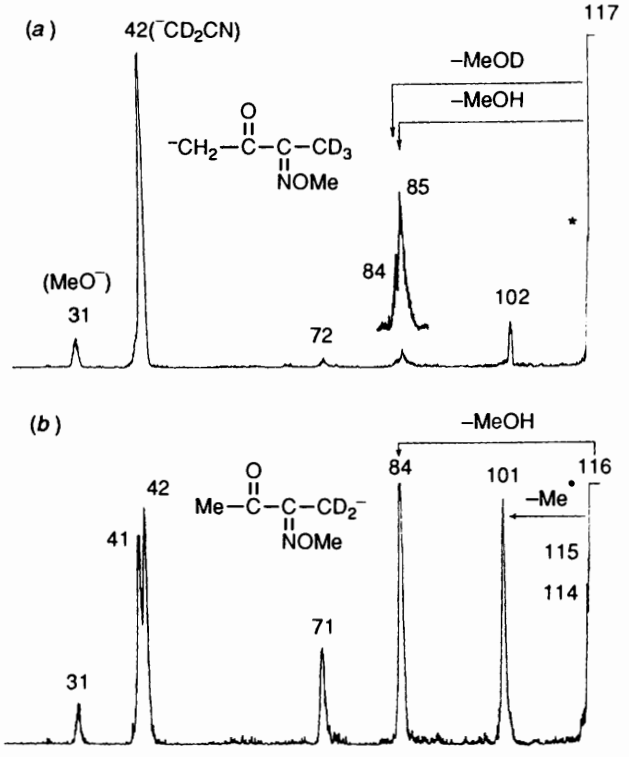
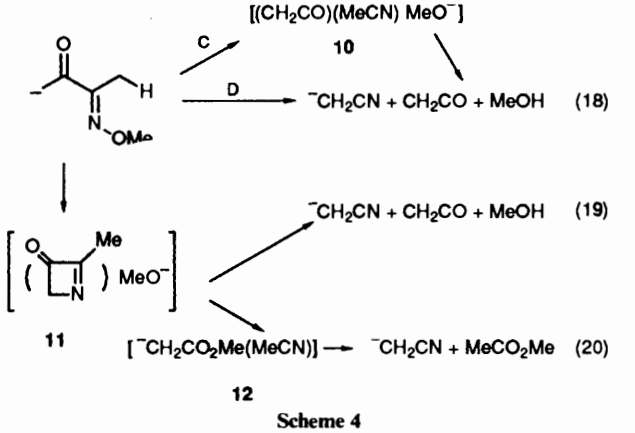


Fig. 4 CA Mass spectra of (*a*) $^-CH_2COC(NOMe)CD_3$ and (*b*) $MeCOC(NOMe)CD_2^-$. VG ZAB 2HF instrument. * In spectrum (*a*) the peaks at *m/z* 116 and 115 are unresolved.

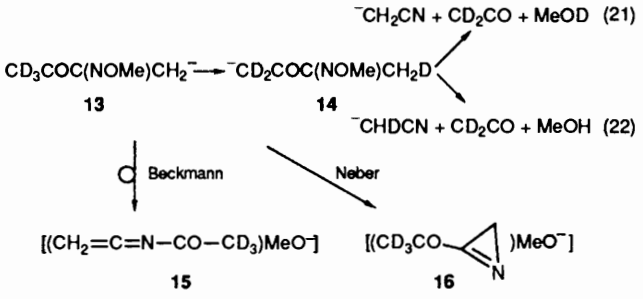
as expected, totally different from those of the α-oximino ketones. The characteristic fragmentations are losses of R^3, and R^3OH, together with formation of $[(R^2 - H)CN]^-$. For example, the appropriate processes from $[MeCOC(NOCD_3)Me - H]^-$ are the loss of $CD_3^{\bullet}$ [to form $(MeCOC(NO^{\bullet})Me - H)^-$] the loss of CD_3OH, and the formation of $^-CH_2CN$.

(*a*) *The formation of* $[(R^2 - H)CN]^-$ *ions.* The first possibility to be considered is whether the ions $[(R^2 - H)CN]^-$ are formed by a Beckmann or Neber rearrangement [cf. eqn. (5)]. Several pertinent observations can be made from a consideration of the data collected in Table 3, *viz.* (*i*) the two ions $[MeCOC(NOMe)R^2 - H]^-$ (R^2 = H and Ph) yield $[(R^2 - H)CN]^-$ as base peak: these ions *cannot* be formed by Beckmann or Neber rearrangements [*cf.* eqn. (5)], and (*ii*) only those neutrals which may deprotonate to form enolate $[(R^1 - H)^-COC(NOMe)R^2]$ yield $[(R^2 - H)CN]^-$ ions (*i.e.* the reaction does not occur when R^1 = Ph).



Scheme 4

Let us therefore examine the proposition that $[(R^2 - H)CN]^-$ ions originate *solely* from an enolate ion, and use the example of MeCOC(NOMe)Me (Table 3) and its three



deuteriated analogues (Table 3 and Fig. 4) as the test case. The probable fragmentations of the enolate ion are summarised in Scheme 4. Cleavage (route C), could form the disolvated ion complex **10** which could decompose to yield $^-CH_2CN$ [eqn. (18)]. Alternatively, this process could be concerted [route D, eqn. (18)]. The other possibilities involve cyclisation to **11**, which can either deprotonate and undergo a retro reaction [eqn. (19)], or a substitution/retro reaction *via* **12** followed by deprotonation [eqn. (20)].

Three of these processes involve the elimination of ketene and methanol; the fourth loss of methyl acetate. Since $^-CH_2CN$ gives the base peak of the spectrum, the eliminated neutral(s) may well be detectable by a neutral reionisation experiment.[22] We have obtained NRMS data using the MS 50 TA instrument. The spectrum is very weak and the only peaks of relevance were due to $MeOH^{+\bullet}$ and its decomposition products. Peaks were not detected due to either $CH_2CO^{+\bullet}$ or $MeCO_2Me^{+\bullet}$, but small peaks would almost certainly be lost in background noise. Unfortunately, the formation of methanol cannot be used as definitive evidence in favour of any process which involves loss of (CH_2CO + MeOH), since loss of methanol is itself observed [*cf.* Fig. 4].

Fragmentation through intermediate **10** may be discounted, since such an intermediate should undergo competitive deprotonation processes to yield HC_2O^- and $^-CH_2CN$ [ΔH°_{acid} (CH_2CO) and (CH_3CN) are 1527[23] and 1560[11] kJ mol^{-1} respectively; and the electron affinitiy of $HC_2O^{\bullet}$ is larger than that of $^{\bullet}CH_2CN$; 2.350[23] and 1.543[24] eV respectively]: the ion HC_2O^- gives a peak less than 5% in abundance. Similarly, that reaction which proceeds through ion complex **12** may be discounted, since such an intermediate must yield $^-CH_2CO_2Me$ as well as $^-CH_2CN$: no $^-CH_2CO_2Me$ is observed [ΔH°_{acid} (CH_3CN) and (CH_3CO_2Me) are 1560[11] and 1557[11] kJ mol^{-1} respectively; and the electron affinity of $^{\bullet}CH_2CO_2Me$ is larger than that of $^{\bullet}CH_2CN$; 1.80[25] and 1.543[24] eV respectively]. Therefore, if the enolate ion is the *sole* precursor of $^-CH_2CN$ then the formation occurs by the concerted process shown in eqn. (18), and/or the cyclisation/retro process of eqn. (19).

Definitive information is forthcoming from the spectra (Table 3, Fig. 4) of the (M − H)$^-$ and (M − D)$^-$ ions derived from $CD_3COC(NOMe)Me$ and $MeCOC(NOMe)CD_3$. The major ions are the enolate species $^-CD_2COC(NOMe)Me$ and $^-CH_2COC(NOMe)CD_3$. The spectra [Table 3, Fig. 4(*a*)] of these ions show *specific* formation of $^-CH_2CN$ and $^-CD_2CN$ respectively. In contrast, the carbanions $CD_3COC(NOMe)CH_2^-$ and $MeCOC(NOMe)CD_2^-$ yield $^-CH_2CN/^-CHDCN$ and $^-CD_2CN/^-CHDCN$ respectively, demanding that some D^+ (or H^+ as appropriate) transfer has preceded or accompanied fragmentation. This evidence indicates that when the enolate ion is the first formed species it is the sole precursor of $[(R^2 - H)CN]^-$ [see route D eqn. (18), and eqn. (19)].

The situation is much more complex when the alternative carbanion is the first formed species. Consider, for example, the decomposition of **13**. If fragmentation occurs specifically through enolate **14** (following D^+ transfer) as shown in eqns.

(21) and (22) then $^-CH_2CN$ and ^-CHDCN should occur in the ratio 1:2 in the absence of an isotope effect. Similarly, $MeCOC(NOMe)CD_2^-$ should form $^-CD_2CN$ and ^-CHDCN is the ratio 1:2. Experimentally, the ratios are *both* precisely 1:0.82 (Table 3 and Fig. 4). We propose that these ratios can be rationalised by two competing reactions producing the same product ion: *i.e.* (*i*) the major reaction is proceeding through the enolate [*e.g.* eqns. (21) and (22)], and (*ii*) a minor process which requires no D^+ (or H^+) transfer, *i.e.* a Beckmann rearrangement through **15** or the corresponding Neber rearrangement through **16**. We cannot differentiate between these two possibilities: either may form the product ion by deprotonation/elimination (*i.e.* to form $^-CH_2CN$ + CD_2CO + MeOD) or by nucleophilic displacement (yielding $^-CH_2CN$ + CD_3CO_2Me). The experimental abundance ratios suggest the competitive enolate and Beckmann/Neber processes occur in the approximate ratio 2:1.

$$PhC\bar{O}C{=}NOMe \longrightarrow [(PhCOCN)MeO^-] \longrightarrow (C_6H_4)^-COCN + MeOH \quad (23)$$

$$^-CH_2COC(NOMe)Me \longrightarrow MeCOC(NOMe)CH_2^-$$

17 **18**

$$[(CH_2{=}C{=}NCOMe)MeO^-] \longrightarrow CH_2{=}C{=}NCOCH_2^- + MeOH \quad (24)$$

(*b*) *The loss of* R^2OH. Consideration of data in Table 3 indicates that there must be a number of different mechanisms operating for the loss of MeOH (or CD_3OH). For example, $PhC\bar{O}C$ = NOMe loses MeOH as shown in eqn. (23). But, as before, the most interesting system is MeCOC(NOMe)Me. The spectra of the labelled derivatives (Table 3, Fig. 4) show that for loss of MeOH, it is $MeCOC(NOMe)CH_2^-$ that is the decomposing ion, and that enolate $^-CH_2COC(NOMe)Me$ must undergo H^+ transfer prior to loss of MeOH. In particular, $CD_3COC(NOMe)CH_2^-$ and $MeCOC(NOMe)CD_2^-$ respectively lose MeOD and MeOH *specifically*, while $^-CD_2COC(NOMe)Me$ and $^-CH_2COC(NOMe)CD_3$ lose MeOH and MeOD in the respective ratios 1:1.4 and 1:0.35 (calculated 1:2 and 2:1 for no isotope effect). These values are consistent with the operation of a small deuterium isotope effect, and we propose that the loss of methanol involves the Beckmann (or Neber) rearrangement both directly from **18** and indirectly *via* **17** [the Beckmann rearrangement is shown in eqn. (24)].*

Conclusions

1. The rearrangements outlined above are the most complex yet recorded for any class of closed shell negative ions. In a number of the cited cases, it has not been possible (with available experimental evidence) to determine a specific and exclusive mechanism for that particular reaction (*e.g.* Beckmann *vs.* Neber).

2. However, there is no evidence that deprotonated α-oximino ketones undergo the Beckmann rearrangement on collisional activation. The condensed phase Beckmann rearrangement of this system produces a carboxylic acid [eqn. (2)], and a carboxylate anion is indeed a major rearrangement product in the gas phase. Yet this ion is not formed by a Beckmann process but by a characteristic four-centre cyclisation [eqn. (6)]. Such reactions yield the broadest dish-shaped peaks yet reported for negative ions: presumably a function of (*i*) the four centre transition state, and (*ii*) the large reverse activation energy of the process (primarily due to the large electron affinity of $RCO_2^•$ [*e.g.* EA ($MeCO_2^•$) = 3.32 eV].†

3. In contrast, it seems that the Beckmann (or related Neber) rearrangement does occur for the corresponding deprotonated α-oximino ketone *O*-methyl ethers, although the rearrangement is not the dominant decomposition pathway. For example, MeCOC(NOMe)Me deprotonates to form $^-CH_2COC(NOMe)Me$ and $MeCOC(NOMe)CH_2^-$ in the ratio 3:1. The enolate ion $^-CH_2COC(NOMe)Me$ fragments principally to yield $^-CH_2CN$ [eqns. (18) and/or (19)], while $MeCOC(NOMe)CH_2^-$ loses MeOH, *via* a Beckmann (or Neber) rearrangement [*e.g.* eqn. (24)]. The product ions give gaussian peaks {electron affinities are much smaller than those of the carboxylate species outlined above [*e.g.* EA($^•CH_2CN$) = 1.543 eV]}.[24]

Experimental

Collisional activation mass spectra (MS/MS) were recorded using a Vacuum Generators ZAB 2HF mass spectrometer operating in the negative chemical-ionization mode.[30] All slits were fully open to obtain maximum sensitivity and to minimize energy resolution effects.[31] The chemical ionization slit was used in the ion source, ionizing energy 70 eV (tungsten filament); ion source temperature 180 °C, accelerating voltage 7 kV. Deprotonation of all neutrals was effected by H_2N^- (from NH_3). The indicated source pressure of NH_3 was 1×10^{-5} Torr (1 Torr = 133.332 Pa.). The substrate pressure (liquids introduced through the septum inlet at 150 °C; solids through the direct probe with no heating) was typically 5×10^{-7} Torr. The estimated total pressure in the ion source is 10^{-1} Torr. The pressure of helium in the second collision cell was 2×10^{-7} Torr measured by an ion gauge situated between the electric sector and the second collision cell. This produced a decrease in the main beam signal of *ca.* 10%, and corresponds to essentially single collision conditions.

Consecutive collision induced dissociation spectra (MS/MS/MS) and charge reversal MS/MS/MS spectra were measured with a Kratos MS 50 TA instrument previously described.[32] Neutral substrates were deprotonated by MeO^- (from MeONO)[33] in a Kratos Mark IV chemical ionization source: ion source temperature 100 °C, electron energy 280 eV, emission current 500 μA and accelerating voltage 8 kV. Samples were introduced through an all glass heated inlet system at 100 °C. The indicated source pressure of substrate was 2×10^{-5} and of methyl nitrite 1×10^{-6} Torr, giving an estimated source pressure of *ca.* 10^{-1} Torr. The indicated pressure of helium in the collision cells was 2×10^{-6} Torr giving a decrease in the main beam signal of 30%.

Preparation of Aldoximes and α-Oximino Ketones.—The following aldoximes [RCOC(NOH)H] are known, and were prepared by a general method:[34] R = Me,[35] Pr,[36] Pr^i,[36] Bu^t[36] and Ph.[37] The following α-oximino ketones [$R^1COC(NOH)R^2$] are known and were prepared by a general procedure:[38] R^1 = R^2 = Me;[39] R^1 = Me, R^2 = Et;[40] R^1 = Me, R^2 = Pr;[41] R^1 = Me, R^2 = Pr^i;[42] R^1 = Me, R^2 = Bu;[43] R^1 = Me, R^2 = Bu^i;[44] R^1 = Me, R^2 = COMe;[45] R^1 = Me, R^2 = Ph;[46] R^1 = Et, R^2 = Me;[47] R^1 = Pr, R^2 = Et;[38] R^1 = Ph, R^2 = Me;[48] and R^1 = R^2 = Ph.[49]

4-*Methylhexan*-2,3-*dione* 3-*ketoxime* [$MeCOC(NOH)Bu^s$],

* The CA mass spectrum of the (source formed) product ion *m/z* 82 is [*m/z* (loss) abundance]: 41(MeCN)13 and 40(CH_2CO)100. This is consistent with structure $CH_2{=}C{=}NCOCH_2^-$, *i.e.* $CH_2{=}C{=}NCOCH_2^- \longrightarrow [^-CH_2CN(CH_2CO)]$ which decomposes to both $^-CH_2CN$ + CH_2CO, and HC_2O^- + MeCN.

† Calculated by the thermodynamic cycle,[26] ΔH°_{acid} ($MeCO_2H$) = DE($MeCO_2$–H) + IE(H^+) – EA($MeCO_2^•$). Thus 1457[27] = 443.5[28] + 1312[29] – EA. EA = 299 kJ mol^{-1} = 3.32 eV.

was prepared from 4-methylhexan-2-one[50] by the general procedure[38] in 40% yield, b.p. 54–56 °C/0.2 mmHg. The compound is unstable on exposure to the atmosphere. $M^{+\cdot}$ (found) = 143.0939, $C_7H_{13}NO_2$ requires *M*, 143.0946; δ_H(60 MHz, $CDCl_3$) 1.0–1.3 (6 H, m), 1.4–2.1 (3 H, m) and 2.33 (3 H, s); δ_C(90 MHz, $CDCl_3$), 12.35 (CH_3), 16.18 (CH_3), 19.25 (CH_3), 25.76 (CH_2), 44.72 (CH), 149.53 (C=N), 162.27 (C=O).

Preparation of Methyl Ethers.—The following aldoxime methyl ethers [RCOC(NOMe)H] were prepared by reported procedures: R = Me,[51] and R = Ph.[52] The listed α-oximino ketone methyl ethers [R^1COC(NOMe)R^2] are known, and were prepared by the general procedure outlined below: R^1 = R^2 = Me;[53] R^1 = Me, R^2 = Et;[54] R^1 = Et, R^2 = Me.[55]

General procedure. The α-oximino ketone (30 mmol) in anhydrous tetrahydrofuran (10 cm^3) was added dropwise, under nitrogen, to sodium hydride (32 mmol, 80%, 0.92 g) in tetrahydrofuran (20 cm^3) and the mixture was stirred for 15 min, maintaining the temperature at 0 °C. Methyl iodide (35 mmol, 5.0 g) was added, the mixture was heated under reflux for 2 h, cooled to 0 °C, and aqueous hydrogen chloride (2 mol dm^{-3}, 15 cm^3) was added. The aqueous layer was extracted with diethyl ether (3 × 20 cm^3), the ethereal extract washed with aqueous sodium hydroxide (5%, 15 cm^3), aqueous sodium chloride (saturated, 20 cm^3) and dried ($MgSO_4$). Removal of the solvent followed by distillation of the residue gave the appropriate α(methyl)oximino ketone (yields 50–80%).

1-*Phenylpropan*-1,2-*dione* 1-(O-*methyloxime*) [MeCOC(NOMe)Ph] was prepared by the above procedure in 67% yield; b.p. 68–70 °C/0.1 mmHg (Found: C, 67.8; H, 6.25; N, 7.9%; $M^{+\cdot}$ = 177.0797. $C_{10}H_{11}NO_2$ requires: C, 67.8; H, 6.3; N, 7.8%; *M*$^{+\cdot}$ = 177.0790); δ_H($CDCl_3$) 2.5 (3 H, s), 4.06 (3 H, s) and 7.4 (5 H, s).

1-*Phenylpropan*-1,2-*dione* 2-(O-*methyloxime*) [PhCOC(NOMe)Me] was prepared by the above procedure in 62% yield; b.p. 52–54 °C/0.04 mmHg (Found: C, 68.0; H, 6.1%; $M^{+\cdot}$ = 177.0796; $C_{10}H_{11}NO_2$ requires C, 67.8; H, 6.3%; *M*$^{+\cdot}$ = 177.0789); δ_H($CDCl_3$) 2.16 (3 H, s), 4.06 (3 H, s), 7.5 (3 H, m), 8.0 (2 H, m).

Labelled Compounds.—$C_6D_5COC(NOH)Me$, $CD_3COC(NOH)Ph$, $C_6D_5COC(NOH)Ph$, and (2,4,6-[$^2H_3$]-phenyl)COC(NOH)Ph were available from a previous study.[10]

1,1,1-[$^2H_3$]*Butan*-2,3-*dione* 3-*oxime* [$CD_3COC(NOH)Me$], and 1,1,1-[$^2H_3$]*pentan*-2,3-*dione* 3-*oxime* [$CD_3COC(NOH)Et$], were prepared by respective exchange of butan-2-one and pentan-2-one with D_2O/NaOD,[18] followed by conversion to the oxime.[38] (D_3 = 90% in both cases.)

4,4-[$^2H_2$]*Pentan*-2,3-*dione* 3-*oxime* [$MeCOC(NOH)CD_2Me$]. 1,1-[$^2H_2$]Ethanol[56] was converted into 1,1-[$^2H_2$]ethyl iodide,[57] which in turn was converted into ethyl 2-(1,1-[$^2H_2$]-ethyl)-3-oxobutanoate,[58] 4,4-[$^2H_2$]pentan-2-one[58] and finally 4,4-[$^2H_2$]pentan-2,3-dione 3-oxime.[38] (D_2 = 98%.)

5,5,5-[$^2H_3$]*Pentan*-2,3-*dione* 3-*oxime* [$MeCOC(NOH)CH_2CD_3$] was prepared as above using 2,2,2-[$^2H_3$]ethanol (D_3 = 98%).

3,3,3-[$^2H_3$]-1-*Phenylpropan*-1,2-*dione* 2-*oxime* [$PhCOC(NOH)CD_3$] was prepared from 1,1,3,3,3-[$^2H_5$]-1-phenylpropan-2-one by the standard route.[38] (D_3 = 90%.)

1,1,1-[$^2H_3$]*Butan*-2,3-*dione* 3-(O-*methyloxime*) [$CD_3COC(NOMe)Me$]. 1,1,1-[$^2H_3$]Butan-2-one was converted first to the oximino ketone[38] and then to the methyl ether using the standard procedure recorded above (D_3 = 96%).

4,4,4-[$^2H_3$]*Butan*-2,3-*dione* 3-(O-*methyloxime*) [$MeCOC(NOMe)CD_3$]. The reaction[58] of ethyl 3-oxobutanoate with [$^2H_3$]methyl iodide gave ethyl-2-([$^2H_3$]methyl)-3-oxobutanoate,[5] which on hydrolysis/decarboxylation[59] gave 4,4,4-[$^2H_3$]-butan-2-one,[5] which was converted to the α-oximino ketone[38] and then to the methyl ether using the standard procedure recorded above (D_3 = 98%).

Butan-2,3-*dione* 3-(O-[$^2H_3$]*methyloxime*) [$MeCOC(NOCD_3)Me$]. Butan-2,3-dione 3-oxime was converted to the labelled methyl ether using [$^2H_3$]methyl iodide (D_3 = 99%).

1-[$^2H_1$]-2-*Phenyl*-2-*oxoethanal* O-*methyloxime* [PhCOC(NOMe)D]. 1-[$^2H_1$]-2-Phenyl-2-oxoethanal oxime (D_1 = 95%) was prepared by a reported route,[53] except that D_2O was used as solvent (in place of H_2O). The aldoxime was converted to the methyl ether by the general procedure (outlined above) using methyl iodide (D_1 = 95%).

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References

1 E. Beckmann, *Chem. Ber.*, 1887, **20**, 1507.
2 G. Donamura and W. Z. Heldt, *Org. React.*, 1969, **11**, 1.
3 P. T. Lansbury and N. R. Mancuso, *Tetrahedron Lett.*, 1965, 2445.
4 A. Maquestiau, Y. van Haverbeke, C. de Meyer, C. Duthoit, P. Meyrant and R. Flammang, *Nouv. J. Chim.*, 1979, **3**, 517; A. Maquestiau, Y. van Haverbeke, R. Flammang and P. Meyrant, *Org. Mass Spectrom.*, 1980, **15**, 80.
5 G. W. Adams, J. H. Bowie and R. N. Hayes, *J. Chem. Soc., Perkin Trans. 2*, 1989, 2159; 1990, 1279.
6 D. J. Cram, *Fundamentals of Carbanion Chemistry*, Academic Press, New York and London, 1965, p. 249.
7 A. Werner and A. Piguet, *Chem. Ber.*, 1904, **37**, 4295; A. H. Blatt, *Chem. Rev.*, 1933, **12**, 215; A. H. Blatt and R. P. Barnes, *J. Am. Chem. Soc.*, 1934, **56**, 1148.
8 A. F. Ferris, *J. Org. Chem.*, 1959, **24**, 580; A. F. Ferris, G. S. Johnson and F. E. Gould, *J. Org. Chem.*, 1960, **25**, 1813.
9 G. W. Adams and J. H. Bowie, unpublished observations.
10 J. H. Bowie and S. Janposri, *Org. Mass Spectrom.*, 1976, **11**, 1290.
11 J. E. Bartmess, J. A. Scott and R. T. McIver, *J. Am. Chem. Soc.*, 1979, **101**, 6047.
12 R. A. J. O'Hair, S. Gronert, K. E. Karrigan, V. M. Bierbaum, C. H. DePuy and J. H. Bowie, *Int. J. Mass Spectrom. Ion Processes*, 1989, **90**, 295.
13 J. E. Bartmess, *The 1987 Gas Phase Acidity Scale*, Univ. of Tennessee.
14 J. S. Shannon, *Aust. J. Chem.*, 1962, **15**, 265.
15 R. A. J. O'Hair, S. Gronert, C. H. DePuy and J. H. Bowie, *J. Am. Chem. Soc.*, 1989, **111**, 3105.
16 J. H. Bowie and T. Blumenthal, *J. Am. Chem. Soc.*, 1975, **97**, 2959; J. E. Szulejko, J. H. Bowie, I. Howe and J. H. Beynon, *Int. J. Mass Spectrom. Ion Phys.*, 1980, **13**, 76.
17 P. C. H. Eichinger, R. N. Hayes and J. H. Bowie, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1815.
18 M. B. Stringer, J. H. Bowie and J. L. Holmes, *J. Am. Chem. Soc.*, 1986, **108**, 3888.
19 G. J. Currie, M. B. Stringer, J. H. Bowie and J. L. Holmes, *Aust. J. Chem.*, 1987, **40**, 1365.
20 J. H. Bowie, *J. Am. Chem. Soc.*, 1973, **95**, 5795.
21 J. H. Bowie, *Mass Spectrom. Rev.*, 1990, **9**, 349.
22 P. O. Danis, C. Wesdemiotis and F. W. McLafferty, *J. Am. Chem. Soc.*, 1983, **105**, 7454; P. C. Burgers, J. L. Holmes, A. A. Mommers and J. K. Terlouw, *Chem. Phys. Lett.*, 1983, **102**, 1.
23 J. M. Oakes, M. E. Jones, V. M. Bierbaum and G. B. Ellison, *J. Phys. Chem.*, 1983, **87**, 4810.
24 S. Moran, H. B. Ellis, D. J. DeFrees, A. D. McLean and G. B. Ellison, *J. Am. Chem. Soc.*, 1987, **109**, 5996.
25 A. H. Zimmerman, K. J. Reed and J. I. Brauman, *J. Am. Chem. Soc.*, 1977, **99**, 7203.
26 C. H. DePuy, V. M. Bierbaum and R. Damrauer, *J. Am. Chem. Soc.*, 1984, **106**, 4051.
27 R. W. Taft, unpublished observations.
28 S. W. Benson, *Thermochemical Kinetics*, John Wiley & Sons, New York and London, 1968.

29 D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churley and R. L. Nuttall, *J. Phys. Chem. Ref. Data 11*, Suppl. 1, 1982.
30 J. K. Terlouw, P. C. Burgers and H. Hommes, *Org. Mass Spectrom.*, 1979, **14**, 307.
31 P. C. Burgers, J. L. Holmes, A. A. Mommers and J. E. Szulejko, *J. Am. Chem. Soc.*, 1984, **106**, 521.
32 D. J. Burinsky, R. G. Cooks, E. K. Chess and M. L. Gross, *Anal. Chem.*, 1982, **54**, 295; M. L. Gross, E. K. Chess, P. A. Lyon, F. W. Crow, S. Evans and H. Tudge, *Int. J. Mass Spectrom. Ion Phys.*, 1982, **42**, 574.
33 D. P. Ridge and J. L. Beauchamp, *J. Am. Chem. Soc.*, 1974, **96**, 3595.
34 W. Sharp and F. S. Spring, *J. Chem. Soc.*, 1948, 1862.
35 P. Freon, *Ann. Chim.*, 1939, **11**, 460.
36 A. L. Green and H. J. Smith, *Biochem. J.*, 1958, **68**, 28.
37 B. B. Day, *J. Chem. Soc.*, 1914, 1043.
38 A. F. Ferris, *J. Org. Chem.*, 1959, **24**, 1726.
39 W. L. Semon and V. R. Damerell, *Org. Syn.*, Coll. Vol. 2, 1945, 205.
40 V. Meyer and J. Zublin, *Chem. Ber.*, 1878, **11**, 323.
41 G. Panzio, *Gazz. Chim. Ital.*, 1921, **51**, 213.
42 O. Diels and H. Jest, *Chem. Ber.*, 1902, **35**, 3292.
43 A. F. Ferris, *J. Org. Chem.*, 1960, **25**, 12.
44 F. Treadwell and B. Westenberger, *Chem. Ber.*, 1882, **15**, 2788.
45 J. E. Zanetti, *Gazz. Chim. Ital.*, 1893, **23**, 303.
46 H. Rheinboldt and O. Schmidt-Dumont, *Ann. Chim.*, 1925, **444**, 113.
47 E. Janecke, *Chem. Ber.*, 1899, **32**, 1100.
48 L. Claisen and O. Manasse, *Chem. Ber.*, 1889, **22**, 529.
49 J. Meisenheimer, *Chem. Ber.*, 1921, **54**, 3206.
50 E. P. Kohler, *Am. Chem. J.*, 1907, **28**, 510.
51 H. Rupe and S. Kessler, *Chem. Ber.*, 1909, **42**, 4718.
52 L. Avogadro, *Gazz. Chim. Ital.*, 1926, **56**, 713.
53 M. Ceresole, *Chem. Ber.*, 1883, **16**, 834.
54 M. Taniewski and R. Lachowicz, *Roczniki Chemi*, 1973, **47**, 2089.
55 Y. Kuroda and M. Kimura, *Bull. Chem. Soc. Jpn.*, 1963, **36**, 464.
56 L. Freedman and A. T. Jurewicz, *J. Org. Chem.*, 1968, **33**, 1254.
57 A. I. Vogel, *Textbook of Practical Organic Chemistry*, 3rd edn., Longmans and Green, 1957, p. 719.
58 W. B. Renfrow, *J. Am. Chem. Soc.*, 1944, **66**, 144.

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