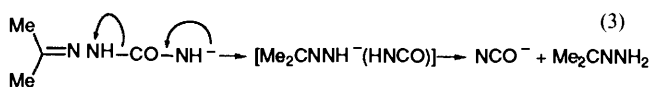
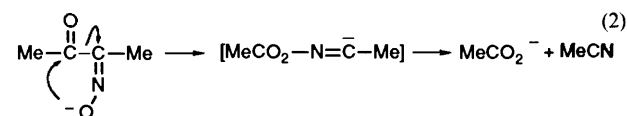
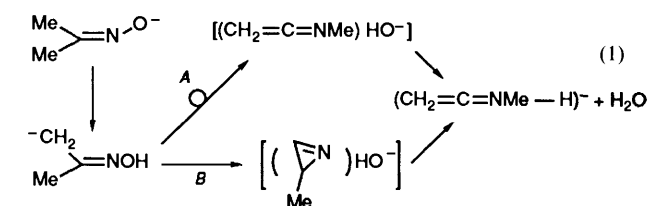


## Rearrangement Reactions of Deprotonated Hydrazones in the Gas Phase

Gregory W. Adams,<sup>a</sup> John H. Bowie,<sup>a</sup> Roger N. Hayes<sup>b</sup> and Michael L. Gross<sup>b</sup><sup>a</sup> Department of Organic Chemistry, The University of Adelaide, South Australia, 5001<sup>b</sup> Department of Chemistry, University of Nebraska, Lincoln, NE, 68585, USA

Evidence is presented which suggests that deprotonated hydrazones undergo a negative ion Beckmann rearrangement, for example,  ${}^{-}\text{CH}_2(\text{Me})\text{C}=\text{NNMe}_2 \longrightarrow [(\text{CH}_2\text{C}=\text{NMe})\text{Me}_2\text{N}^{-}] \longleftrightarrow [(\text{CH}_2=\text{C}=\text{NMe})^{-}\text{Me}_2\text{N}^{\bullet}] \longrightarrow {}^{-}\text{CH}_2\text{CN} + \text{Me}_3\text{N}$ . A number of fragmentations not involving skeletal rearrangement are also observed including a characteristic elimination of methane, *e.g.*  ${}^{-}\text{CH}_2(\text{Me})\text{C}=\text{NNMe}_2 \longrightarrow [(\text{CH}_2(\text{Me})=\text{C}-\text{N}=\text{NMe})\text{Me}^{-}] \longrightarrow \text{CH}_2(\text{Me})=\text{C}-\text{N}=\text{NCH}_2^{-} + \text{CH}_4$ .

Although many even-electron organic negative ions fragment by simple and predictable processes,<sup>1-3</sup> there are those which because of their structural features decompose following skeletal rearrangement. Aliphatic oximes fall into the latter category: their deprotonated form eliminates water on collisional activation and it has been proposed that this occurs by a negative ion Beckmann process following proton transfer [*e.g.* route A, eqn. (1)], although the Neber process [*e.g.* route B, eqn. (1)] is an alternative but less likely process.<sup>4</sup> However not all oximes and their derivatives undergo this reaction. For example,  $\alpha$ -oximino ketones undergo a four centre cyclisation/elimination [eqn. (2)],<sup>5</sup> while deprotonated semicarbazones undergo the simple fragmentation shown in eqn. (3).<sup>6</sup>



Since there is such variation in the fragmentation behaviour of negative ions derived from oximes, we have extended our investigations to hydrazone derivatives. This paper addresses the following question. Do protonated hydrazones behave like simple oximes in undergoing Beckmann (or Neber) type reactions, or do they undergo some other characteristic rearrangement?

## Results and Discussion

The collisional activation mass spectra of a variety of deprotonated hydrazones together with some deuteriated derivatives are either recorded in Table 1 or illustrated in Figs. 1-4. The spectra of all unlabelled species were measured with an MS 50 TA spectrometer, while deuteriated derivatives were studied using a VG ZAB 2HF instrument. Tandem mass spectra (MS/MS/MS) of selected daughter ions are collected in Tables 2 and 3. Consideration of all these data collectively indicates that there are some unexpected fragmentations (*e.g.* the pronounced loss of  $\text{CH}_4$ , which we will discuss later) together with a number of

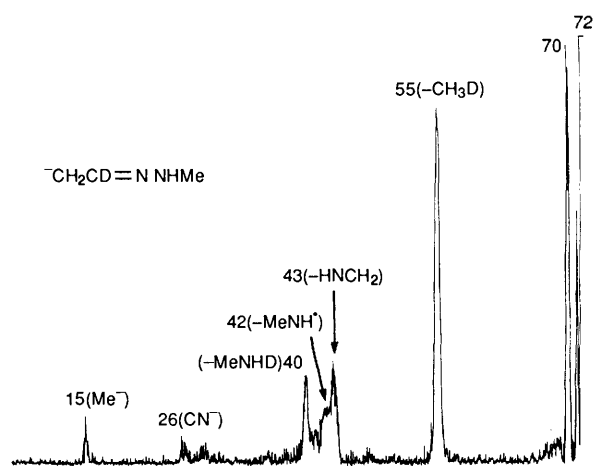
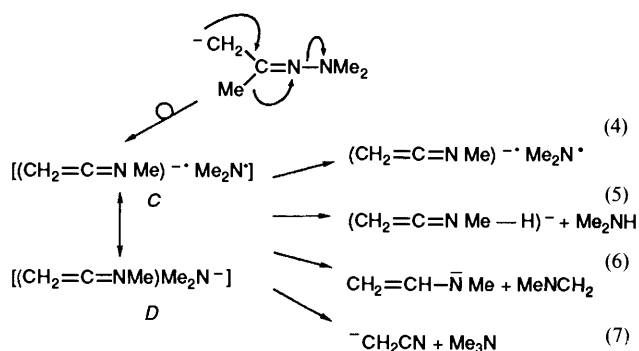


Fig. 1 Collisional activation mass spectrum of  ${}^{-}\text{CH}_2\text{CD}=\text{NNHMe}$ . VG ZAB 2HF instrument.

decompositions which have analogies to those described previously.<sup>4</sup> Rather than dealing with all these spectra individually, we will summarise the fragmentations, illustrating particular features by reference to selected spectra.

All ions studied have the general structure  $[\text{R}^1\text{R}^2\text{C}=\text{NR}^3-\text{H}]^{-}$ . Deprotonation was effected by  $\text{MeO}^{-}$  in the MS 50 TA instrument and with  $\text{NH}_2^{-}$  in the VG ZAB 2HF spectrometer. When  $\text{R}^1$  and  $\text{R}^2$  are alkyl, and  $\text{R}^3 = \text{Me}_2\text{N}$ , deprotonation takes place exclusively at  $\text{R}^1$  and/or  $\text{R}^2$ ,  $\alpha$  to the double bond [see labelled compounds  $(\text{CD}_3)_2\text{C}=\text{NNMe}_2$  (Fig. 3), also  $(\text{MeCD}_2)_2\text{C}=\text{NNMe}_2$  (Table 1)]. When  $\text{R}^1 = \text{H}$ ,  $\text{R}^2 = \text{alkyl}$  and  $\text{R}^3 = \text{NH}_2$  or  $\text{NHMe}$ , deprotonation again occurs predominantly at  $\text{R}^2$ ; minor deprotonation (generally <15%) occurs at  $\text{R}^1$  and  $\text{R}^3$  but does not contribute to fragmentation.



Scheme 1

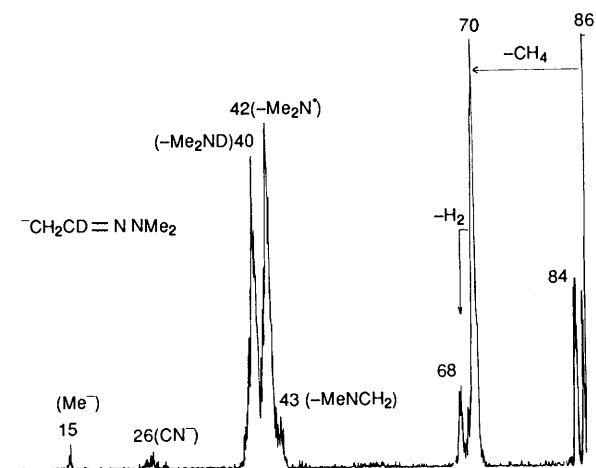


Fig. 2 Collisional activation mass spectrum of  $^{-}\text{CH}_2\text{CD}=\text{NNMe}_2$ . VG ZAB 2HF instrument.

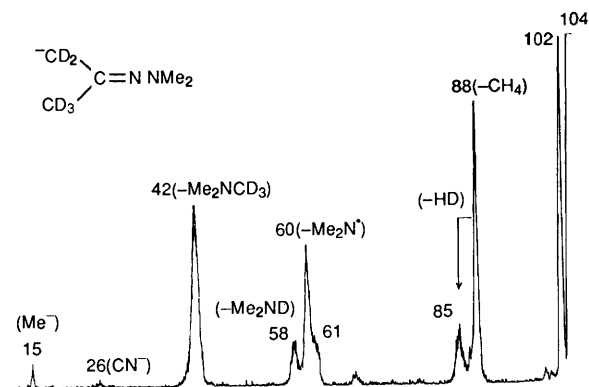
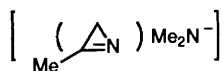


Fig. 3 Collisional activation mass spectrum of  $^{-}\text{CD}_2(\text{CD}_3)\text{C}=\text{NNMe}_2$ . VG ZAB 2HF instrument.

**Rearrangement Processes of Deprotonated Hydrazones.**—All spectra show peaks which are formed following rearrangement of the  $(\text{R}^1\text{R}^2\text{C}=\text{NR}^3\text{-H})^-$  system. Such fragmentations include the losses of  $(\text{R}^3)$ ,  $(\text{R}^3\text{-H})$  (for  $\text{R}^3=\text{Me}_2\text{N}$  or  $\text{MeNH}$ ),  $\text{R}^3\text{H}$ ,  $(\text{R}^1\text{R}^3)$  and  $(\text{R}^2\text{R}^3)$ . Specific fragmentations are listed in Table 1 and illustrated in Figs. 1–4. We propose that these processes are a consequence of the Beckmann rearrangement. We consider that the alternative Neber rearrangement is a less likely possibility,\* but it cannot be totally excluded on the available evidence. In Scheme 1 (*cf.* also Fig. 3) we use a specific example to rationalise the rearrangement reactions. The Beckmann rearrangement yields an intermediate complex  $[\text{C} \leftrightarrow \text{D}]$  which may eliminate  $\text{Me}_2\text{N}^+$  [eqn. (4)], undergo deprotonation with elimination of  $\text{Me}_2\text{NH}$  [eqn. (5)], hydride transfer [eqn. (6)],† or effect the  $\text{S}_{\text{N}}2$  reaction shown in eqn. (7).

There are several ways in which the Beckmann reactions shown in eqns. (4)–(7) differ from those of deprotonated oximes.

\* The Neber process should produce the intermediate:



In principle, this system could decompose by processes analogous to those shown in eqns. (4)–(7), indeed the ionic products formed by losses of  $\text{Me}_2\text{NH}$  and  $\text{Me}_3\text{N}$  should be the same as those shown in eqns. (5) and (7). On balance, we consider the Beckmann processes to be more kinetically favoured than the Neber rearrangement.

† Simple amines are known to fragment through neutral/hydride ion complexes.<sup>7</sup>

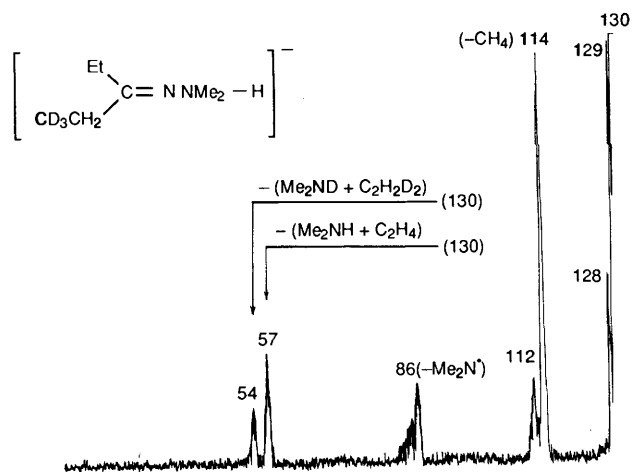
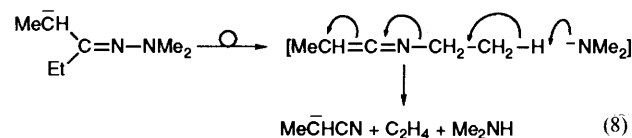


Fig. 4 Collisional activation mass spectrum of  $[\text{Et}(\text{CD}_3\text{CH}_2)\text{C}=\text{NNMe}_2\text{-H}]^-$ . VG ZAB 2HF instrument.

Consider the Beckmann intermediate  $[(\text{CH}_2=\text{C}=\text{NMe})\text{HO}]^-$  formed from  $[\text{Me}_2\text{C}=\text{NOH-H}]^-$ . This species eliminates  $\text{H}_2\text{O}$  to give the base peak of the spectrum, while the  $\text{S}_{\text{N}}2$  process involving loss of  $\text{MeOH}$  is minor in comparison.<sup>4</sup> In contrast, the intermediate shown in Scheme 1 undergoes a major  $\text{S}_{\text{N}}2$  process [eqn. (7)], while the deprotonation reaction is a minor process. Indeed of all the spectra listed in Table 1, only two, those of  $[\text{Me}_2\text{C}=\text{NNH}_2\text{-H}]^-$  and  $[\text{Me}_2\text{C}=\text{NNMe}_2\text{-H}]^-$  show loss of  $\text{R}^3\text{H}$ . In addition, oxime intermediates do not lose  $\text{HO}^+$ , whereas loss of  $(\text{R}^3)$  is a standard reaction of hydrazones. This feature cannot be ascribed to basicity differences [*e.g.*  $\Delta G_{\text{acid}}^\circ(\text{NH}_3) = 1657$ ;<sup>8</sup>  $(\text{H}_2\text{O}) = 1607 \text{ kJ mol}^{-1(9)}$ ], therefore it must be a function of the nature of the decomposing intermediate, which to a major extent depends upon the electron affinities of the two parts of each intermediate. In the oxime, the electron affinity of  $\text{HO}^+$  is relatively high ( $176 \text{ kJ mol}^{-1(9)}$ ) so the intermediate will look like  $[(\text{CH}_2=\text{C}=\text{NMe})\text{HO}]^-$ . However the electron affinities of the amine radicals are much lower, *e.g.*  $\text{NH}_2^{\cdot}$  (72),<sup>10</sup>  $\text{MeNH}^{\cdot}$  (43)<sup>8</sup> and  $\text{Me}_2\text{N}^{\cdot}$  ( $37 \text{ kJ mol}^{-1}$ ).<sup>8</sup> Thus the intermediate in Scheme 1 is more likely to resemble the radical anion/radical *C* than the anion/neutral contributor *D*. Perhaps this is the reason for the differences in the Beckmann processes of oximes and hydrazones.



It is of interest now to consider reactions analogous to the  $\text{S}_{\text{N}}2$  process [eqn. (7)] for unsymmetrical hydrazones [*i.e.* compare the relative losses of  $(\text{R}^1\text{R}^3)$  and  $(\text{R}^2\text{R}^3)$  in Table 1]. There are two series of ions (listed in Table 1) which show the same general trend, *viz.*  $[\text{Me}(\text{alkyl})\text{C}=\text{NNH}_2\text{-H}]^-$  and  $[\text{Me}(\text{alkyl})\text{C}=\text{NNMe}_2\text{-H}]^-$ . When  $\text{R}^1 = \text{Me}$  and  $\text{R}^2 = \text{Et}$ , the loss of  $^{\cdot}\text{EtR}^3$  is some five times greater than loss of  $\text{MeR}^3$ , but this value decreases with elaboration of  $\text{R}^2$ . This dramatic effect cannot be a function of the migratory aptitude of the alkyl substituent. The answer lies in Fig. 4, where it can be seen that the loss is accompanied by an appreciable deuterium isotope effect ( $\text{H/D } 2.0$ ), *i.e.* the process involves the removal of H from a terminal methyl group in the rate determining step of the reaction. Thus when  $\text{R}^1$  and/or  $\text{R}^2 \geq \text{Et}$ , an  $\text{E}2$  reaction [*e.g.* eqn. (8) and *cf.* Fig. 4] operates in competition with the  $\text{S}_{\text{N}}2$

**Table 1** Collisional activation mass spectra of deprotonated  $R^1R^2C=NR^3$  species

Neutral			Loss											Formation					
R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	H	H <sub>2</sub>	HD	CH <sub>4</sub>	(CH <sub>4</sub> + H <sub>2</sub> )	Et <sup>*</sup>	Pr <sup>*</sup>	(R <sup>3</sup> ) <sup>*</sup>	(R <sup>3</sup> - H)	R <sup>3</sup> H	(R <sup>1</sup> R <sup>3</sup> )	(R <sup>2</sup> R <sup>3</sup> )	Ph <sup>-</sup>	CHN <sub>2</sub> <sup>-</sup>	CN <sup>-</sup>	R <sup>3-</sup>	Me <sup>-</sup>
Me	Me	NH <sub>2</sub>	18	75						32		12	100					8	10
Me	Et	NH <sub>2</sub>	78	92						19			15	100				8	8
Me	Bu	NH <sub>2</sub>	32	73						22	28		48	100				8	9
Pr	Bu	NH <sub>2</sub>	100	48					30	17	22		28	26					
Pr	Ph	NH <sub>2</sub>	100	62					28										
H	Me	NHMe		100		85							8			18			2
D	Me	NHMe	see Fig. 1																
H	CD <sub>3</sub>	NHMe	85	24	100								10			20	1		2
H	Et	NHMe	84		100								18			15			
H	Pr	NHMe	58		100								18			12			
H	Bu	NHMe	71		100								22			12			
Me	Me	NHMe	95		38	16				48	42		100						1
H	Me	NMe <sub>2</sub>	45		100	15				55	5		55				1		2
D	Me	NMe <sub>2</sub>	see Fig. 2																
H	CD <sub>3</sub>	NMe <sub>2</sub> <sup>a</sup>	59	4	100					59	8		64				1		3
H	Pr	NMe <sub>2</sub>	52		100	8				10 <sup>a</sup>	10 <sup>a</sup>		82						
H	Bu	NMe <sub>2</sub>	30		78	8				15 <sup>a</sup>	15 <sup>a</sup>		100						
Me	Me	NMe <sub>2</sub>	100	21	62	13				12	15	4	18						2
CD <sub>3</sub>	CD <sub>3</sub>	NMe <sub>2</sub>	see Fig. 3																
Me	Et	NMe <sub>2</sub>	100	18	40	12				8	4		3	15					2
Me	Pr	NMe <sub>2</sub>	70	32	100	22		26		22	18		16	22					2
Me	Bu	NMe <sub>2</sub>	45	28	100	28			20	18	25		18	14					1
Me	Bu <sup>*</sup>	NMe <sub>2</sub>	80	32	100	28			22	22	15		18	18					1
Et	Et	NMe <sub>2</sub>	75	41	100	15				12 <sup>b</sup>	12 <sup>b</sup>		46						3
MeCD <sub>2</sub>	MeCD <sub>2</sub>	NMe <sub>2</sub>		35	100	9				11 <sup>b</sup>	11 <sup>b</sup>		54						3
Et	CD <sub>3</sub> CH <sub>2</sub>	NMe <sub>2</sub>	see Fig. 4																
Et	Pr	NMe <sub>2</sub>	28	32	100	20		8	8	10			28	14					2
Pr	Pr	NMe <sub>2</sub>	28		100	9		32		25	24		48						2
Pr	Bu	NMe <sub>2</sub>	35		100	10		5	15 <sup>c</sup>	18	15 <sup>c</sup>		26	24					1
Bu	Bu	NMe <sub>2</sub>	30		100	8				10	12		28						1
Me	Ph	NMe <sub>2</sub>	100		10					12	10			3	8				
Et	Ph	NMe <sub>2</sub>	100		12					8	8			2	4				
Pr	Ph	NMe <sub>2</sub>	100		10					10	9			3	5				

<sup>a</sup> Parent ion is an (M - D) species. <sup>b</sup> Unresolved. <sup>c</sup> Both losses correspond to 43 amu.

**Table 2** Collisional activation MS/MS/MS data for selected product ions from deprotonated hydrazones

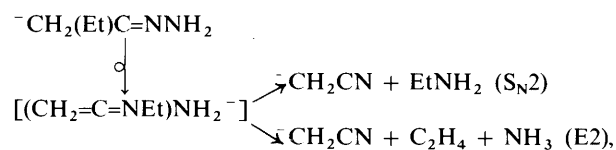
Precursor ion ( <i>m/z</i> )	Product ion loss ( <i>m/z</i> )	Product ion spectrum <i>m/z</i> (loss) abundance
(MeCH=NNMe <sub>2</sub> - H) <sup>-</sup> (85)	Me <sub>2</sub> N <sup>*</sup> (41)	40 (H) 100
[Me(Pr)C=NNMe <sub>2</sub> - H] <sup>-</sup> (127)	Me <sub>2</sub> N <sup>*</sup> (83)	40 (C <sub>3</sub> H <sub>7</sub> ) 100
	Me <sub>3</sub> N (68)	67 (H) 25, 66 (H <sub>2</sub> ) 100, 52 (CH <sub>4</sub> ) 78
(Pr <sub>2</sub> C=NNMe <sub>2</sub> - H) <sup>-</sup> (155)	'Me <sub>2</sub> (Pr)N <sup>*</sup> (68) <sup>a</sup>	67 (H) 28, 66 (H <sub>2</sub> ) 100, 52 (CH <sub>4</sub> ) 71
EtCHCN (68)		67 (H) 26, 66 (H <sub>2</sub> ) 100, 52 (CH <sub>4</sub> ) 60, 39 (C <sub>2</sub> H <sub>5</sub> ) 0.5, 26 (C <sub>3</sub> H <sub>6</sub> ) 0.5, 15 (C <sub>3</sub> H <sub>3</sub> N) 0.1
(Bu <sub>2</sub> C=NNMe <sub>2</sub> - H) (183)	'Me <sub>2</sub> (Bu)N <sup>*</sup> (82)	81 (H) 20, <sup>b</sup> 80 (H <sub>2</sub> ) 100, 52 (C <sub>2</sub> H <sub>6</sub> ) 78
PrCHCN (82)		81 (H) 15, 80 (H <sub>2</sub> ) 100, 52 (C <sub>2</sub> H <sub>6</sub> ) 75

<sup>a</sup> Weak spectrum—peaks less than 5% of the base peak will be lost in baseline noise. <sup>b</sup> Not resolved.

process. The relative ratios of S<sub>N</sub>2 and E2 reactions for those ions listed in Table 1 (when R<sup>1</sup> and/or R<sup>2</sup> ≥ Et) are not known, but the MS/MS/MS data recorded in Table 2 indicate that the product anion is the same in both cases, *i.e.* a deprotonated nitrile.

A slightly different trend is noted for the competitive 'Beckmann' S<sub>N</sub>2 and E2 reactions for oximes.<sup>4</sup> In systems [Me(R)C=NOH-H]<sup>-</sup>, the following ratios are observed for the losses of 'ROH' and MeOH; R = Et (4:1), R = Pr (5:1), R = Bu ('BuOH' is lost exclusively). Thus it seems that the extent of the E2 reaction increases with elaboration of R. These results are consistent with those reported for competitive bimolecular S<sub>N</sub>2 and E2 ion molecule reactions.<sup>11,12</sup> The S<sub>N</sub>2 process is generally the more exothermic of the two, yet the E2 reaction is normally that observed in the gas phase (the opposite is generally true in the condensed phase). Thus the gas phase reaction

is kinetically controlled. The same trend is observed for the hydrazone systems described here. For example in the model case

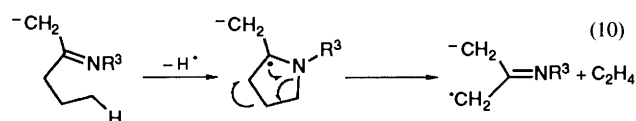
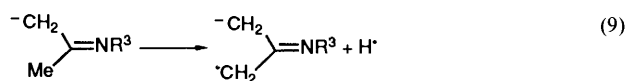


the S<sub>N</sub>2 process is 56 kJ mol<sup>-1</sup> more favoured than the E2 process [ $\Delta H_f^\ddagger$  values of EtNH<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and NH<sub>3</sub> are -50, +52 and -46 kJ mol<sup>-1</sup> respectively],<sup>13</sup> yet the E2 process is clearly operating.

*Simple Cleavage Processes and Related Reactions.*—When R<sup>1</sup> and R<sup>2</sup> are both alkyl, loss of H<sup>\*</sup> is always pronounced.

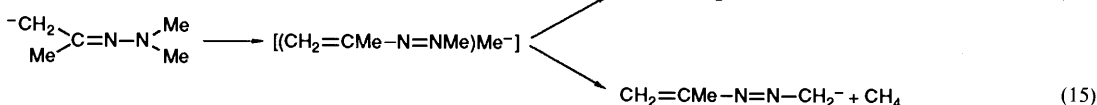
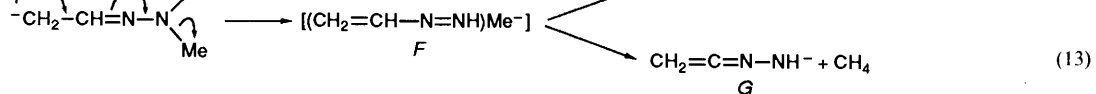
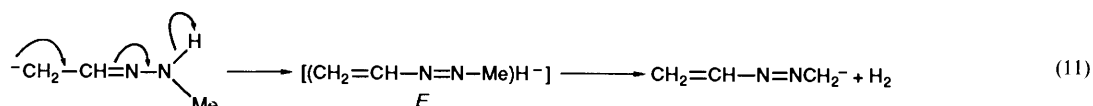
**Table 3** Collisional activation MS/MS/MS data for product ions formed by loss of methane from deprotonated hydrazones.

Precursor ion ( <i>m/z</i> )	Product ( <i>m/z</i> )	Product ion spectrum <i>m/z</i> (loss) abundance
(MeCH=NNHMe-H) <sup>-</sup> (71)	(55)	54 (H) 8, 53 (H <sub>2</sub> ) 18, 40 (NH) 100, 26 (C <sub>2</sub> H <sub>3</sub> N) 17
(MeCH=NNMe <sub>2</sub> -H) <sup>-</sup> (85)	(69)	67 (H <sub>2</sub> ) 100, 41 (CH <sub>2</sub> N) 70
(Me(Pr)C=NNMe <sub>2</sub> -H) <sup>-</sup> (127)	(111)	109 (H <sub>2</sub> ) 100, 95 (CH <sub>4</sub> ) 18, 83 (CH <sub>2</sub> N) 68
(Me(Bu)C=NNMe <sub>2</sub> -H) <sup>-</sup> (141)	(125)	123 (H <sub>2</sub> ) 100, 109 (CH <sub>4</sub> ) 8, 97 (CH <sub>2</sub> N) 28
(Me(Bu <sup>s</sup> )C=NNMe <sub>2</sub> -H) <sup>-</sup> (141)	(125)	123 (H <sub>2</sub> ) 100, 109 (CH <sub>4</sub> ) 8, 97 (CH <sub>2</sub> N) 27

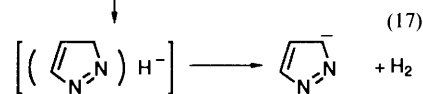
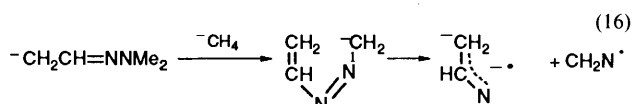


Examination of Figs. 1 and 2 [also (MeCD<sub>2</sub>)<sub>2</sub>C=NNMe<sub>2</sub> (Table 1)] indicates formation of a radical anion of the type shown in eqn. (9). Whenever R<sup>1</sup> and R<sup>2</sup> are alkyl and either substituent is ≥ Pr, 'β-cleavage' occurs to the double bond, e.g. a propyl substituent loses 'C<sub>2</sub>H<sub>5</sub>', butyl loses 'C<sub>3</sub>H<sub>7</sub>', but ethyl does not lose 'CH<sub>3</sub>' (see Table 1). This is a standard two-step reaction which has been observed for a variety of systems including oximes<sup>4</sup> and which has been described in detail.<sup>3</sup> A particular example is shown in eqn. (10).

When R<sup>3</sup> = MeNH or Me<sub>2</sub>N, the base peak of the spectrum is usually produced by loss of methane. In order to examine the mechanism of this loss, we (i) examined the spectra of a number of labelled compounds (Table 1, Figs. 1–3) and (ii) determined MS/MS/MS data for a variety of daughter ions formed by loss of methane (Table 3). The initial clue to the course of this reaction actually came from a cognate process, the loss of H<sub>2</sub>. This process is observed for all spectra, however when R<sup>1</sup> = H and R<sup>3</sup> = MeNH, loss of H<sub>2</sub> occurs to the exclusion of H<sup>+</sup> loss. Labelling studies (see e.g. Fig. 1 and Table 1) indicate that *this* loss of H<sub>2</sub> comes predominantly from the MeNH group. We propose a simple process proceeding through hydride ion intermediate *E* as shown in eqn. (11). Labelling studies suggest similar pathways for the loss of methane. Whenever R<sup>3</sup> = Me<sub>2</sub>N, loss of methane occurs *exclusively* through that group (see Figs. 2 and 3), but when R<sup>3</sup> = MeNH, and R<sup>1</sup> = H, *both* groups are involved. The latter case is illustrated in Fig. 1: here we suggest that intermediate *F* may decompose directly to Me<sup>-</sup>



[eqn. (12)], or Me<sup>-</sup> effects the deprotonation reaction to form product ion *G* [eqn. (13)]. The mass spectrum of *G* is shown in Table 3: the loss of NH<sup>+</sup> to form <sup>-</sup>CH<sub>2</sub>CN is particularly diagnostic. The analogous reactions, for R<sup>3</sup> = Me<sub>2</sub>N, are shown in eqns. (14) and (15) (see also Fig. 3). The only difference is the deprotonation site shown in eqn. (15).

**Scheme 2**

The MS/MS/MS data for daughter ions formed in processes analogous to that shown in eqn. (15), are particularly diagnostic and are recorded in Table 3. The simplest case is shown in Scheme 2. Here, loss of methane, gives rise to *I* which upon collisional activation competitively loses CH<sub>2</sub>N<sup>•-</sup> [eqn. (16)] and H<sub>2</sub> [eqn. (17)]. The latter process is particularly facile and is also a feature of the mass spectra of the hydrazones themselves [see (CH<sub>4</sub> + H<sub>2</sub>) fragments in Table 1 and Fig. 2, also the (CH<sub>4</sub> + HD) fragment in Fig. 3].

In conclusion, the negative ion Beckmann rearrangement does occur for deprotonated hydrazones and the most favoured reactions resulting from this rearrangement are the internal S<sub>N</sub>2 and E2 reactions illustrated in eqns. (7) and (8) respectively. Deprotonated hydrazones also undergo a number of simple cleavage reactions, for example the loss of methane which involves terminal NHMe or NMe<sub>2</sub> substituents.

## Experimental

The collisional activation mass spectra (MS/MS) of all unlabelled

compounds were measured with an MS 50 TA instrument,<sup>14</sup> while the corresponding spectra of deuteriated derivatives were recorded with a VG ZAB 2HF instrument.<sup>15</sup> All tandem MS/MS/MS data were obtained with the MS 50 TA spectrometer.<sup>14</sup> Full details of experimental procedures have been reported.<sup>14,15</sup> The ion  $\text{MeO}^-$  (from  $\text{MeONO}$ )<sup>16</sup> was used as deprotonating agent in MS 50 TA experiments, while  $\text{NH}_2^-$  (from  $\text{NH}_3$ ) was the reagent ion using the VG ZAB 2HF instrument. Helium gas was used as collision gas in both instruments: the collision gas pressure was  $2 \times 10^{-6}$  Torr in one or both collision cells (as appropriate) of the MS 50 TA (giving a reduction in main beam intensity of 30%), and  $2 \times 10^{-7}$  Torr in the second collision of the VG ZAB 2HF (giving a reduction in main beam intensity of 10%).

Hydrazones were prepared from the appropriate ketone and hydrazine hydrate using a standard method.<sup>17</sup> All compounds are known *i.e.* hydrazones from propan-2-one, butan-2-one, pentan-3-one, hexan-2-one, hexan-3-one and butyrophenone.<sup>17</sup>

Methylhydrazones of ethanal,<sup>18</sup> propanal,<sup>19</sup> butanal,<sup>19</sup> pentanal,<sup>19</sup> and propan-2-one,<sup>20</sup> are known compounds prepared from methylhydrazine by a standard procedure.<sup>17</sup> Dimethylhydrazones of ethanal,<sup>21</sup> propanal,<sup>22</sup> butanal,<sup>23</sup> propan-2-one,<sup>24</sup> butan-2-one,<sup>25</sup> 3-methylbutan-2-one,<sup>23</sup> pentan-2-one,<sup>25</sup> pentan-3-one,<sup>25</sup> 4-methylpentan-3-one,<sup>25</sup> heptan-4-one,<sup>23</sup> hexan-2-one,<sup>23</sup> nonan-2-one,<sup>23</sup> acetophenone,<sup>26</sup> propiophenone<sup>26</sup> and butyrophenone<sup>26</sup> are known compounds formed from *N,N*-dimethylhydrazine using a standard method.<sup>17</sup>

**Deuterium-labelled Compounds.**—The [<sup>2</sup>H<sub>6</sub>]propan-2-one hydrazones. A mixture of [<sup>2</sup>H<sub>6</sub>]propan-2-one (20 mmol) and the appropriate hydrazine (20 mmol) was heated under reflux for 6 h. The mixture was cooled to 25 °C, extracted with diethyl ether, the organic extract dried ( $\text{MgSO}_4$ ) and distilled to yield the required [<sup>2</sup>H<sub>6</sub>]propan-2-one hydrazone (yields 75–80%). The products prepared were: [<sup>2</sup>H<sub>6</sub>]propan-2-one hydrazone (b.p. 123–125 °C/760 mmHg; <sup>2</sup>H<sub>6</sub> = 90, <sup>2</sup>H<sub>5</sub> = 8, <sup>2</sup>H<sub>4</sub> = 2%); [<sup>2</sup>H<sub>6</sub>]propan-2-one methyl hydrazone (b.p. 116–118 °C/760 mmHg; <sup>2</sup>H<sub>6</sub> = 90, <sup>2</sup>H<sub>5</sub> = 8, <sup>2</sup>H<sub>4</sub> = 2%); [<sup>2</sup>H<sub>6</sub>]propan-2-one dimethyl hydrazone (b.p. 92–94 °C/760 mmHg; <sup>2</sup>H<sub>6</sub> = 92, <sup>2</sup>H<sub>5</sub> = 8%).

**The [<sup>2</sup>H<sub>3</sub>]- and [<sup>2</sup>H<sub>1</sub>]-ethanal hydrazones.** These compounds were prepared (as above) from [2,2,2-<sup>2</sup>H<sub>3</sub>]ethanal<sup>4</sup> and [1-<sup>2</sup>H<sub>1</sub>]ethanal<sup>27</sup> as appropriate, yields 75–80%. [<sup>2</sup>H<sub>3</sub>]Ethanal methylhydrazone (b.p. 80–82 °C/760 mmHg; <sup>2</sup>H<sub>3</sub> = 95%). [<sup>2</sup>H<sub>3</sub>]Ethanal dimethylhydrazone (b.p. 90–92 °C/760 mmHg; <sup>2</sup>H<sub>3</sub> = 95%). [<sup>2</sup>H<sub>1</sub>]Ethanal methylhydrazone (b.p. 80–82 °C/760 mmHg; <sup>2</sup>H<sub>1</sub> = 99%). [<sup>2</sup>H<sub>1</sub>]Ethanal dimethylhydrazone (b.p. 90–92 °C/760 mmHg; <sup>2</sup>H<sub>1</sub> = 99%).

[1,1,1-<sup>2</sup>H<sub>3</sub>] Pentan-3-one dimethylhydrazone. This compound was prepared by lithiation of butan-2-one dimethylhydrazone followed by reaction with [<sup>2</sup>H<sub>3</sub>]iodomethane using the method of Ludwig.<sup>28</sup> Yield 78%, b.p. 150–152 °C/760 mmHg, <sup>2</sup>H<sub>3</sub> = 99, <sup>2</sup>H<sub>2</sub> = 1%.  $\delta_{\text{H}}$ (60 MHz,  $\text{CDCl}_3$ ) 1.2 (3 H, t), 2.02 (2 H, s), 2.35 (2 H, q) and 2.4 (6 H, s).

[2,2,4,4-<sup>2</sup>H<sub>4</sub>] Pentan-3-one dimethylhydrazone. Exchange of pentan-3-one with  $\text{D}_2\text{O}/\text{Na}^4$  gave [2,2,4,4-<sup>2</sup>H<sub>4</sub>]pentan-3-one (<sup>2</sup>H<sub>4</sub> = 96%) which was converted to the dimethylhydrazone

by the standard procedure in 75% yield, b.p. 150–152 °C/760 mmHg, <sup>2</sup>H<sub>4</sub> = 95, <sup>2</sup>H<sub>3</sub> = 5%.

## Acknowledgements

This work was supported by the Australian Research Council, and the Midwest Center for Mass Spectrometry (NSF Grant CHE 9017250). One of us (G. W. A.) thanks both universities for financial support to allow him to spend a period at Lincoln as an exchange graduate student.

## References

- M. J. Raftery and J. H. Bowie, *Int. J. Mass Spectrom. Ion Processes*, 1988, **85**, 167.
- J. H. Bowie, *Mass Spectrom. Rev.*, 1990, **9**, 349.
- P. C. H. Eichinger and J. H. Bowie, *Int. J. Mass Spectrom. Ion Processes*, 1991, **110**, 123.
- G. W. Adams, J. H. Bowie and R. N. Hayes, *J. Chem. Soc., Perkin Trans. 2*, 1989, 2159; 1990, 1279.
- G. W. Adams, J. H. Bowie and R. N. Hayes, *J. Chem. Soc., Perkin Trans. 2*, 1991, 1809.
- G. W. Adams and J. H. Bowie, *Rapid Commun. Mass Spectrom.*, 1990, **4**, 283.
- M. J. Raftery and J. H. Bowie, *Aust. J. Chem.*, 1988, **41**, 1477.
- G. J. MacKay, R. S. Hemsworth and D. K. Bohme, *Can. J. Chem.*, 1976, **54**, 1624.
- P. A. Schulz, R. D. Mead, P. L. Jones and W. C. Lineberger, *J. Chem. Phys.*, 1982, **77**, 1153.
- C. T. Wickham-Jones, K. M. Ervin and W. C. Lineberger, *J. Chem. Phys.*, 1989, **91**, 2762.
- M. E. Jones and G. B. Ellison, *J. Am. Chem. Soc.*, 1989, **111**, 1645.
- C. H. DePuy, S. Gronert, A. Mullin and V. M. Bierbaum, *J. Am. Chem. Soc.*, 1990, **112**, 8650.
- S. W. Benson, *Thermochemical Kinetics*, John Wiley and Sons, New York, London and Sydney, 1968.
- 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**, 243.
- M. B. Stringer, J. H. Bowie and J. L. Holmes, *J. Am. Chem. Soc.*, 1986, **108**, 3888.
- D. P. Ridge and J. L. Beauchamp, *J. Am. Chem. Soc.*, 1974, **96**, 3595.
- G. Karabatsos and C. E. Osborne, *Tetrahedron*, 1968, **24**, 3361.
- E. Müller and W. Rundel, *Chem. Ber.*, 1956, **89**, 1065.
- B. V. Ioffe, V. S. Stopskii and Z. I. Sergeeva, *Zh. Obshch. Khim.*, 1968, **4**, 986.
- J. A. Barltrop and M. Conlong, *J. Chem. Soc. B*, 1967, 1081.
- F. Klages, *Ann. Chim.*, 1941, **547**, 1.
- G. Karabatsos and R. A. Taller, *Tetrahedron*, 1968, **24**, 3923.
- G. S. Gol'din, T. Siomo and G. S. Shor, *Zh. Obshch. Khim.*, 1970, **6**, 754.
- R. H. Wiley, S. C. Slaymaker and H. Kraus, *J. Org. Chem.*, 1957, **22**, 204.
- G. R. Newkome and D. L. Fishel, *J. Org. Chem.*, 1966, **31**, 677.
- P. A. S. Smith and E. E. Most, *J. Org. Chem.*, 1957, **22**, 318.
- L. C. Leitch, *Can. J. Chem.*, 1955, **33**, 400.
- J. W. Ludwig, M. Newcomb and D. E. Bergbreiter, *J. Org. Chem.*, 1980, **45**, 4666.

Paper 1/057351

Received 12th November 1991

Accepted 9th December 1991