

## Thermal Fragmentations

### V.\* The Conversion of Cyclohexanone Semicarbazone into Cyclohexanone Azine

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The thermal cleavage of cyclohexanone semicarbazone proceeds with the formation of cyclohexanone azine and other products. By extending previous results on the cleavage of bonds between heteroatoms and the C=X (X=O, S) group, the temperature dependence of the ratio of different products can be explained. From the mass spectra obtained from cyclohexanone and acetone semicarbazones it is concluded that  $\alpha$ -cleavage to the C=X group occurs provided the samples do not evaporate prior to fragmentation.

Use of the heated inlet system of a mass spectrometer sometimes results in mass spectra which differ appreciably from those obtained by use of the direct insertion technique. These differences in fragmentation patterns may arise, as pointed out by, *e.g.*, Spitteller,<sup>1</sup> from a thermal excitation of the molecules prior to ionization, caused by the collisions between the molecules and the hot walls of the indirect inlet system. However, in some cases, the application of the two different techniques to one sample results in spectra in which the changes must reflect the fact that different molecules are introduced in the ion source. This means that a thermal reaction takes place in the heated inlet system. A well known reaction of this type is the thermally induced dehydration of alcohols.

An example of a more complicated thermal reaction has recently been published by Waight.<sup>2</sup> It is reported that cyclohexanone semicarbazone (Ia, Fig. 2) admitted *via* the heated inlet system (at 240°C) showed no peak corresponding to the molecular ion at  $m/e$  155, but instead gave an ion at  $m/e$  192 which was claimed to be the molecular ion of cyclohexanone azine (IIa). When the temperature was reduced to 165°C the intensity of the 192 peak decreased, and instead a peak at  $m/e$  155 was observed. These results, taken together with the fact that no peak corresponding to the azine was observed

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when Ia was examined by the direct insertion technique,<sup>2,3</sup> reveals that a transformation occurs in the heated inlet system, prior to ionization.

In a later paper, Blythin and Waight<sup>4</sup> report that the mass spectrum of cyclohexanone azine ((IIa), Fig. 2) is identical with that obtained from the transformed semicarbazone Ia using the heated inlet system at 250°C. This result is not quite in accordance with the information presented by Nakata and Tatematsu,<sup>5</sup> who described both spectra as being *essentially* identical above  $m/e$  40 (neither temperature of the inlet system, nor intensities of peaks, are given). Nakata and Tatematsu observed in the spectrum of the transformed semicarbazone Ia a few extra peaks in the low mass region, and a relatively strong peak at  $m/e$  138, which was not found in the spectrum of IIa. These discrepancies, as well as the failure of the authors to explain the formation of cyclohexanone azine at elevated temperature, led us to reinvestigate the mass spectrum of Ia under different conditions.

In part III of this series<sup>6</sup> it was shown that 1,1-diethyl-4-phenylsemicarbazide, on heating, was cleaved on both sides of the carbonyl group as indicated in Fig. 1 by the vertical wavered lines. If similar fragmentations occur when cyclohexanone semicarbazone (Ia) is heated, the compounds IIIa - VIa

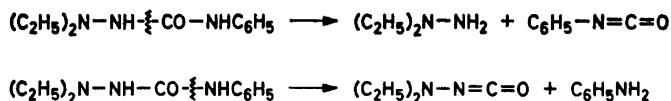


Fig. 1.

(Fig. 2) are formed initially. As IIIa decomposes even at 0°C into IIa and nitrogen-containing by-products<sup>7</sup> of low molecular weight, the scheme depicted in Fig. 2 can explain the conversion of Ia into IIa.

## RESULTS AND DISCUSSION

The results of this investigation led to the following theory. On attempts to introduce the rather non-volatile semicarbazone Ia by way of the heated inlet system, a *low-temperature* fragmentation (reaction 2, Fig. 2, breaking of the C-N amide bond) occurred when the temperature in the sample bottle reached a value between 150 and 180°C. As the resonance form Ia' in Fig. 3 is probably favoured relative to Ia'' due to the effect of conjugation, the C-N amide bond is expected to have less double bond character than the C-N hydrazide bond. In contrast to the semicarbazides<sup>6</sup> therefore, only the weak C-N amide bond is cleaved at low temperatures. The result is that *N*-isocyanatocyclohexylideneamine (Va) and ammonia are introduced into the reservoir of the mass spectrometer instead of Ia. After closing the valve between the sample bottle and the reservoir the equilibrium  $\text{Va} + \text{VIa} \rightleftharpoons \text{Ia}$  is established only if the temperature in the reservoir does not exceed 210°C. However, at this temperature Ia is also able to undergo a *high temperature fragmentation* (reaction 1, Fig. 2, breaking of the C-N hydrazide bond) with formation of cyclohexanone hydrazone (IIIa) and isocyanic acid (IVa).

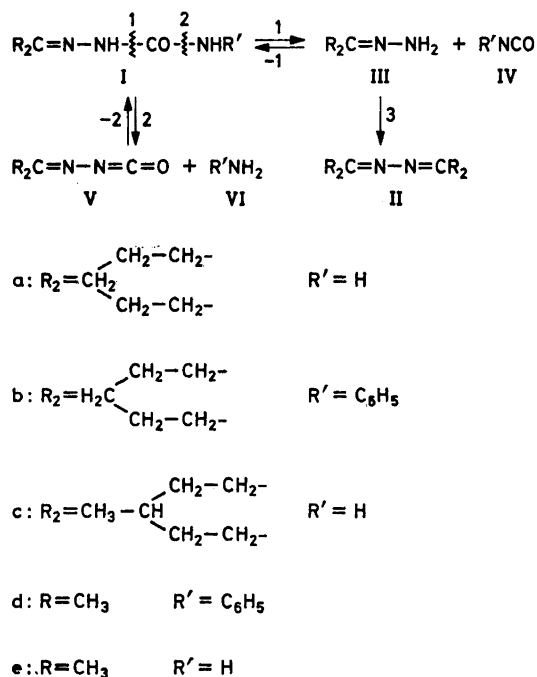


Fig. 2.

This reaction is finally followed by an irreversible conversion of the thermally unstable hydrazone IIIa to cyclohexanone azine (IIa) (reaction 3 of Fig. 2).

During attempts to reproduce the results given by Blythin and Waight,<sup>4</sup> the spectrum of IIa was recorded at various temperatures of the inlet system, to establish the influence of changes in the temperature. Only very small changes were introduced by a variation in temperature from 90 to 250°C. For this reason comparison of the spectrum of IIa (spectrum A of Fig. 4), recorded while the temperature of the inlet system was kept at 250°C, with the spectra of the converted semicarbazone Ia, kept in the 210°C hot reservoir (Fig. 4 (B) and (C)), can be made directly.

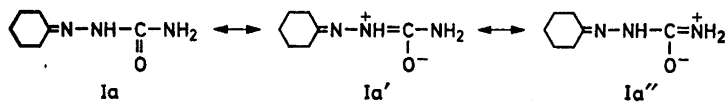
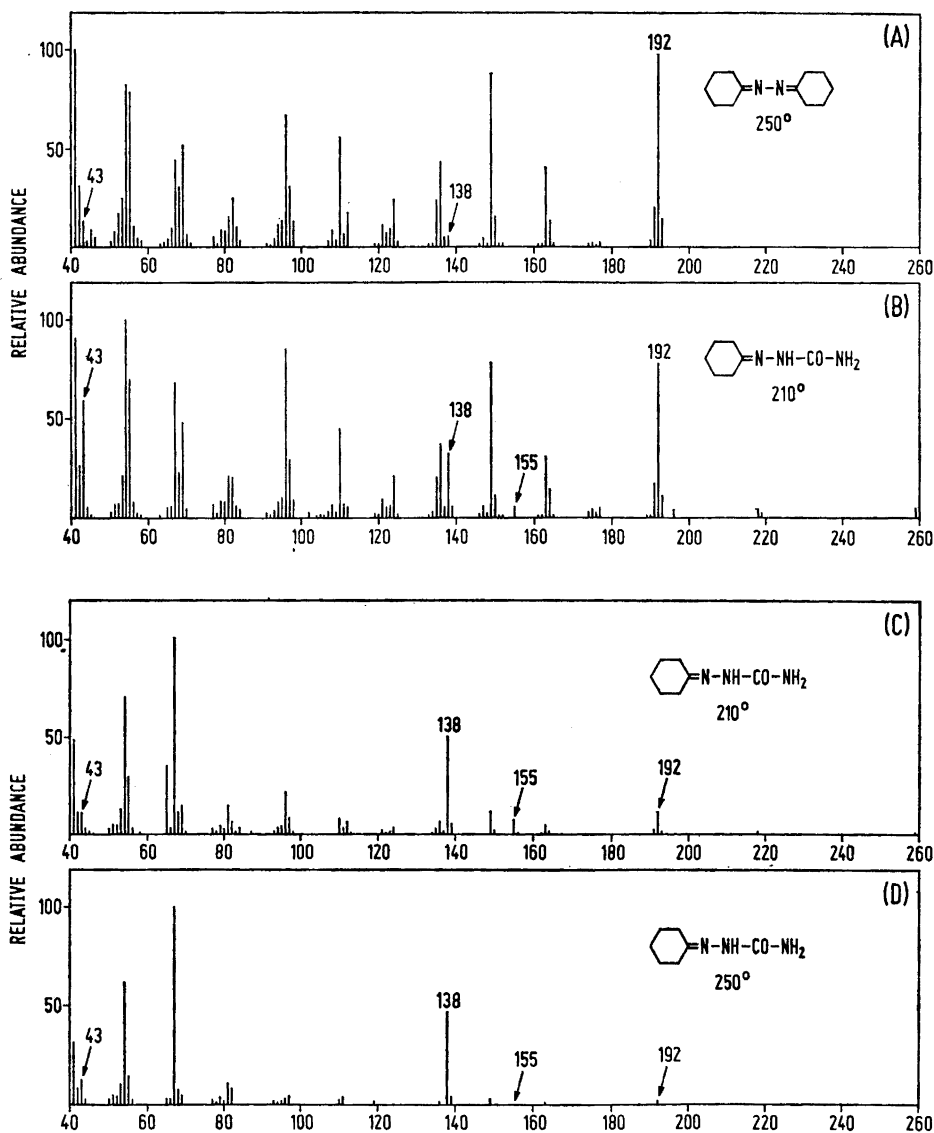


Fig. 3.

When Ia was heated in the sample bottle to a temperature supposed to be about 160°C, the pressure in the 250°C hot reservoir slowly rose, and after ca. 15 min a suitable pressure was obtained. At this time the valve to the sample bottle was closed, and the spectrum presented in Fig. 4 (D) was re-



*Fig. 4.* (A) represents the mass spectrum of cyclohexanone azine (IIa). Introduction of the thermolysis products of Ia into the reservoir (kept at 210°C) produced the different spectra (B) and (C). (C) was recorded as soon as the pressure was suitable. (B) was recorded 15 minutes later. (B) can be interpreted as an equilibrium mixture of IIa, Va, IVa and unchanged Ia. (C) arises from the same compounds before equilibrium was reached. (D) is the spectrum of the thermolysis products from Ia when these were kept at a higher temperature within the reservoir. The spectrum is mainly due to Va.

corded. From the intensities of the characteristic peaks due to IIa (*cf.* spectrum A), it was concluded that only traces of this compound was present. Above  $m/e$  40 the spectrum is dominated by four peaks at  $m/e$  138, 67, 54, and 41 ascribed to Va, which has a composition of  $C_7H_{10}N_2O$  corresponding to the isotopic content of  $m/e$  138 (confirmed by high resolution measurement). The formation of this compound can be explained as the result of the *low-temperature fragmentation* of Ia (reaction 2, Fig. 2), presumably taking place in the sample bottle. The occurrence of this fragmentation is substantiated by a peak at  $m/e$  17 ( $NH_3$ ) of very high intensity. As the spectrum did not change noticeably with time (recordings were made after 5, 10, and 15 min), the reaction  $Ia \rightarrow Va + VIa$  must either be irreversible or be an equilibrium which is displaced very much to the right at  $250^\circ C$ . This point will be treated below.

The experiment was repeated with the same operating conditions as before, but with a lower temperature of the reservoir ( $210^\circ C$ ). After the sample pressure had reached the same value as in the first experiment, the valve to the sample bottle was closed and a spectrum recorded (Fig. 4 (C)). The spectrum is dominated by the same four peaks, with almost the same relative intensity as was found in the spectrum presented in Fig. 4 (D). The content of the azine IIa (peaks at  $m/e$  192, 163, 149 *etc.*) is still low, but higher than that found in (D). An additional peak was found at  $m/e$  155 shown by high-resolution measurement to have a composition corresponding to the molecular ion of Ia. These results demonstrate, that at least three compounds (Ia, IIa and Va) with molecular weights higher than 100 were present. A large peak corresponding to  $NH_3$  (VIa) was also found in this spectrum. The presence of both Va and VIa supports the assumption that a *low-temperature fragmentation* of Ia had occurred, as before.

Accepting for the moment that reaction 2 (Fig. 2) is reversible, and that the forward reaction  $Ia \rightarrow Va + VIa$  is endothermic, the lower temperature of the reservoir will favour a displacement of the equilibrium towards Ia. The result of this displacement is the appearance of the molecular ion of Ia at  $m/e$  155 in spectrum C. The explanation for the increased abundance of the azine, is given later.

The spectrum of the freshly introduced material (Fig. 4 (C)) is changed drastically on standing. A spectrum recorded 15 min later is reproduced in Fig. 4 (B). Comparison of this spectrum to spectrum (A) shows all the characteristic peaks of the azine IIa to be present. However, an examination of spectrum B reveals that the apparent spectrum of IIa is superimposed both a large peak at  $m/e$  43 and the spectrum of Va. On going from spectrum C to spectrum B the intensities of the peaks due to the azine IIa are increased, while at the same time the intensities of the peaks belonging to Va are decreased. Moreover it is seen that, while the intensity of the peak at  $m/e$  43 is increased, the intensity of the peak at  $m/e$  155 (the molecular ion of Ia) remains almost constant. Assuming the reaction  $Ia \rightleftharpoons Va + VIa$  to be reversible, the fact that the combined intensities of the molecular ion of Ia and Va decrease at constant temperature, demonstrates that Ia is, in some way, transformed into products other than Va and VIa.

Exact mass measurement of the doublet at  $m/e$  43 in spectrum B showed, that the peak at the lower mass number is due to  $HNCO$ . Only the intensity

of this peak has been reproduced in spectrum B of Fig. 4. Comparison with spectrum C shows that the fragmentation of Ia or Va can only contribute to a small extent, and IIa, of course, cannot be the precursor of HNCO. Therefore the difference in intensity between  $m/e$  43 in the spectra B and C must originate from the *molecular ion* HNCO<sup>+</sup>, and not from a fragment ion with this composition. The formation of isocyanic acid (IVa) can be explained as the result of a cleavage of the C–N hydrazide bond in the semicarbazone Ia formed at 210°C, *i.e.* the result of a *high-temperature fragmentation* (reaction 1, Fig. 2). No direct evidence for the formation of the postulated cyclohexanone hydrazone (IIIa) has been obtained, but evidence for the easy conversion (even at 0°C) of this compound to the azine IIa (reaction 3, Fig. 2) is found in the literature.<sup>7</sup>

It remains to be explained why only a very small amount of IIa is found in spectrum D (Fig. 4). When Ia is heated in the sample bottle the *low-temperature fragmentation* occurs prior to the vaporisation of this compound. As the fragmentation is not instantaneous, and since the temperature is further increased, a small fraction of Ia may remain when the temperature of the sample bottle has reached a value where the *high-temperature fragmentation* starts. The small amount of IIa found in spectrum D can thus be formed before the reaction products enter the 250°C hot reservoir. The assumption that the reaction Ia → Va + VIa is endothermic is corroborated by the fact that no sign of Ia is found when the temperature of the reservoir is 250°C, thus preventing further formation of IIa.

Additional confirmation of the theory presented above was obtained through the study of the thermal fragmentation of cyclohexanone 4-phenylsemicarbazone (Ib). This compound is expected to be more difficult to thermolyse, as both the C–N hydrazide and the C–N amide bond may have double bond character. To obtain a sufficient monitor pressure the temperature of the sample bottle had to be increased to *ca.* 250°C, while the temperature of the reservoir was kept at 200°C. The molecular weight of Ib is 231, but no peaks were found above  $m/e$  192 (the molecular ion of IIa). As the intensity of the peak due to the molecular ion of Ib is very high (95 % of the base peak) when this compound is introduced through the direct inlet, the absence of a peak at  $m/e$  231 proves that Ib is completely thermolysed when introduced *via* the heated inlet system. Apart from the spectrum of the azine IIa (which had a rather low intensity), the spectrum obtained was composed of the known spectra of Va, VIb,<sup>8</sup> and IVb.<sup>9</sup> The presence of VIb and IVb, and the absence of Ib indicates that breaking of both the C–N amide and the C–N hydrazide bond occurs in the sample bottle.

Thermolysis of Ib also occurred when this compound was examined on a combined gas chromatograph-mass spectrometer furnished with a heated metal block inlet system. Fig. 5 shows the ion current trace from an experiment in which an acetone solution of Ib was injected into a gas chromatograph. The major peaks were scanned, and the results of these scans were the spectra of phenyl isocyanate (IVb), aniline (VIb) and the azine IIa. The detection of the stable compounds IVb and VIb, characteristic of a cleavage on both sides of the carbonyl group, confirms the scheme depicted in Fig. 2.

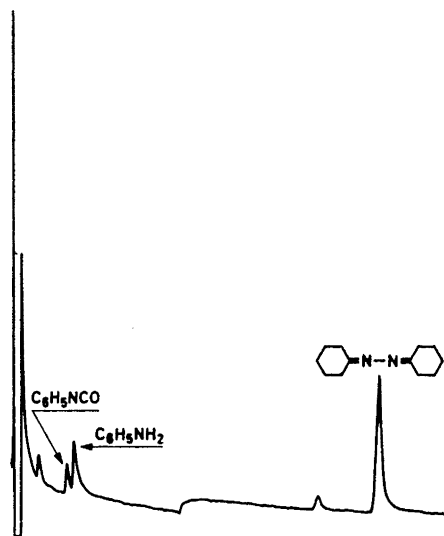


Fig. 5. Ion current trace from an acetone solution of cyclohexanone 4-phenylsemicarbazone (Ib) injected into a combined gas chromatograph-mass spectrometer furnished with a metal block inlet system kept at 300°C.

Further evidence for the formation of Va from cleavage of the C–N amide bond was obtained when 4-methylcyclohexanone semicarbazone (Ic) was heated in the sample bottle, keeping the temperature of the reservoir at 250°C. Comparison of the mass spectrum with spectrum (D) (Fig. 4) showed that the peaks found in the latter spectrum at  $m/e$  138 and 67 were displaced 14 mass units upwards in the spectrum of the thermolysed Ic. Further experiments with Ic were not made as Nakata and Tatematsu<sup>5</sup> have already shown that this compound is able to form 4,4'-dimethylcyclohexanone azine (IIc).

The azine formation is not restricted to semicarbazones derived from cyclic aliphatic ketones, as was evident from the spectrum of the thermolysis products of acetone 4-phenylsemicarbazone (Id). The spectrum of Id obtained by use of the direct insertion technique showed a peak corresponding to the molecular ion at  $m/e$  191, with an intensity of 50% (relative to base peak at  $m/e$  72). The use of the heated all-glass inlet system resulted in a spectrum without any peak at  $m/e$  191; all the peaks present could, however, be explained as molecular or fragment ions of the compounds VIb, IVb, Vd, and IIId (Fig. 2). The correspondence of the peaks at  $m/e$  112 ( $M^+$  of acetone azine (IIId)) and at  $m/e$  98 ( $M^+$  of *N*-isocyanatoisopropylideneamine (Vd)) to  $C_6H_{12}N_2$  and  $C_4H_6N_2O$ , respectively, were shown by accurate mass measurements.

In contrast, the spectra of acetone semicarbazone (Ie) obtained by use of the direct inlet system and the heated all-glass inlet system were much alike, both in the position of the peaks and in their relative intensities. For example, with the use of the direct inlet system the intensity of the molecular ion at

$m/e$  115 was 42 %, whereas with the use of the glass inlet system it was 39 % (both intensities relative to a base peak at  $m/e$  72).

These results demonstrate that formation of azines from semicarbazones may occur when semicarbazones are heated in a sample bottle connected to the inlet system of a mass spectrometer. However, if the temperature in the inlet system is kept as low as possible, thermal fragmentation will occur only when the compounds have a low volatility (Ia, Ib, Ic, and Id). A more volatile compound such as Ie is, however, vaporized before the temperature in the sample bottle is increased to a value where thermal fragmentation occurs, and in such a case a spectrum hardly distinguishable from the one obtained by use of the direct inlet system can be recorded.

### EXPERIMENTAL

With the exception of the results from the combined gas chromatograph-mass spectrometer (GC-MS), all mass spectra were obtained using an AEI MS-902 mass spectrometer operating at 70 eV. The source temperature was kept at 180°C. Exact mass measurements were performed at a resolution of 10.000 (10 % valley definition) using heptacosafuorotributylamine to provide reference masses.

The GC-MS examination of Ib was carried out on a Varian MAT CH 7 combined gas chromatograph-mass spectrometer, equipped with a double-stage separator of the Biemann-Watson type. The mass spectrometer was operated at 70 eV. The ion source temperature was 120°C, and the ionizing current 100  $\mu$ A. The gas chromatograph was a Varian Aerograph 204 B using a 5 ft  $\times$  1/8 in glass column packed with 3 % SE 30 on Chromosorb W. The column temperature was 50–180°C, 6°C/min, and the temperatures of the injector, separator, and interface were 300, 180, and 250°C, respectively. The helium flow rate through the column was 30 ml/min. The GLC trace was given by the ion current at 20 eV.

The compounds were prepared by reported procedures: Cyclohexanone semicarbazone (Ia),<sup>10</sup> cyclohexanone azine (IIa),<sup>11</sup> cyclohexanone 4-phenylsemicarbazone (Ib),<sup>12</sup> 4-methylcyclohexanone semicarbazone (Ic),<sup>13</sup> acetone 4-phenylsemicarbazone (Id),<sup>13</sup> acetone semicarbazone (Ie),<sup>14</sup> and the identities were confirmed by melting points and infrared spectra.

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