Behaviour of Semicarbazones in a Mass Spectrometer

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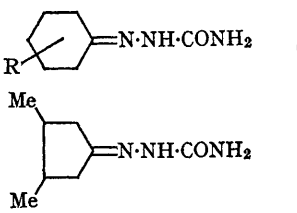
A RECENT paper by Djerassi and his co-workers[1] on the mass spectral fragmentation of semicarbazones prompted us to report our own observation of the behaviour of cycloalkanone semicarbazones in a mass spectrometer.

By using a Hitachi RMU-6D mass spectrometer with a direct inlet system, cyclohexanone semicarbazone (I) gave a mass spectrum including peaks at *m/e* 155 (corresponding to the molecular ion), 138, 112, and 111. However, an entirely different spectral pattern was obtained when the compound was introduced into the same instrument through an all-glass heating inlet system. In this spectrum the peak at *m/e* 155 was absent, and there was an apparent molecular peak at *m/e* 192, and other intense peaks at *m/e* 163, 149, 138, 136, 124, 110, 96, 81, 69, 67, 55, 54, and 41.

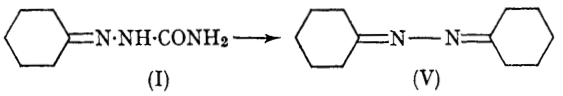
3- or 4-Methylcyclohexanone semicarbazones[2]



		M
	(I; R = H)	155
	(II; R = 3-Me)	169
	(III; R = 4-Me)	169
	(IV)	169

(II or III) showed similar behaviour, the corresponding molecular peak appearing at *m/e* 220. Since the substitution of one methyl group at the cyclohexanone ring causes a shift of the molecular peak by 28 mass units, these abnormal spectra should originate from compounds that have two cyclohexane moieties. In the case of (I), this was

confirmed by accurate mass measurement* of the peak at *m/e* 192 (obs. *m/e* 192·162, calc. for $C_{12}H_{20}N_2$, *m/e* 192·163). These results suggest that the following reaction occurs in the mass spectrometer.



(I) (V)

To substantiate this transformation, pure cyclohexanone azine (V) was prepared[3] from cyclohexanone and hydrazine and its spectrum was compared with that of (I). Both spectra above *m/e* 40 are essentially identical. A few extra peaks observed in the low mass region of (I) may probably be ascribed to some other by-products of low molecular weight from the above reaction. A relatively strong peak of (I) at *m/e* 138 is accounted for by assuming the loss of ammonia from the semicarbazone molecule. Therefore, it can be concluded that cyclohexanone semicarbazone (I) is converted into cyclohexanone azine (V) in the mass spectrometer when a heating inlet system is used.

This novel reaction also takes place with 3,4-dimethylcyclopentanone semicarbazone (IV).† The intense molecular peak appeared at *m/e* 220, instead of at *m/e* 169, the molecular weight of (IV). The elemental composition of this peak was established by accurate mass measurement* (obs. *m/e* 220·194, calc. for $C_{14}H_{24}N_2$, *m/e* 220·193).

(*Received, January 2nd*, 1967; *Com.* 002.)

* The measurement of high-resolution spectra by Mr. Hitoshi Tsuyama, Hitachi Central Research Laboratory, is gratefully acknowledged.

† The sample was kindly supplied by Dr. Yoshinari Kato, Faculty of Pharmaceutical Sciences, Nagoya City University.

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[2] A. I. Vogel, *J. Chem. Soc.*, 1938, 1323.
[3] W. H. Perkin, Jr., and S. G. P. Plant, *J. Chem. Soc.*, 1924, **125**, 1503.