Journal of Organometallic Chemistry, 96 (1975) C35–C37

Preliminary communication

PSEUDOTROPYLIUM AND CYCLOPENTADIENYL IONS IN THE MASS SPECTRA OF TRI-*N*-METHYLBORAZINES

R. HARRY CRAGG*
The Chemical Laboratory, University of Kent at Canterbury (Great Britain)
and ALAN F. WESTON
Department of Molecular Sciences, University of Warwick (Great Britain)
(Received June 16th, 1975)

Summary

Ion kinetic energy spectra of a series of tri-*N*-methylborazines suggest the possible formation of cyclopentadienyl-like ions, by metastable decomposition in the first field free region of a mass spectrometer, from their tropylium-like ions.

The decomposition of the tropylium ion in the first field free (drift) region of a mass spectrometer, to form a cyclopentadienyl ion, was first reported by Jennings [1]. In a more recent paper [2] the energies associated with the process, from a large number of benzyl compounds, have been reported. It was concluded that the decomposing $C_7H_7^+$ ions which gave energy releases of about 30 meV were tropylium in nature, those which gave releases of about 46 meV were benzyl and those in between possessed a mixture of the two structures.

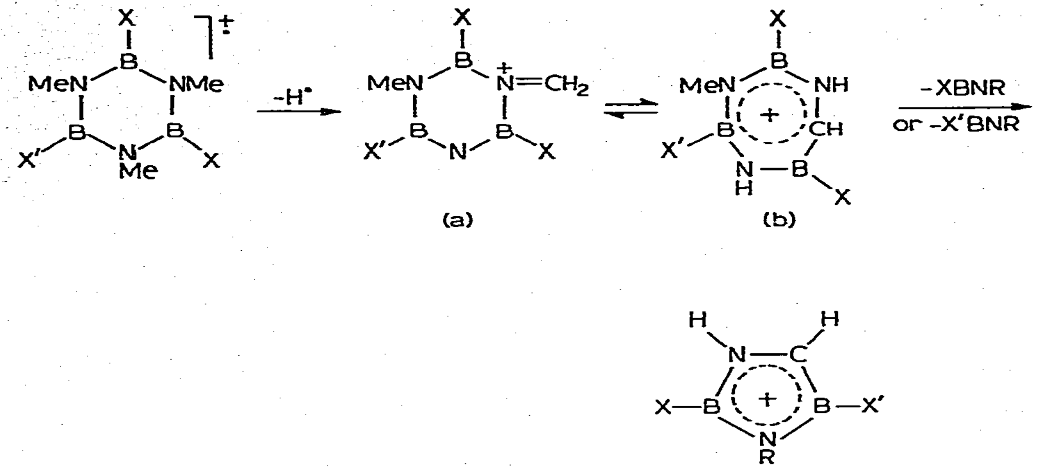
Borazines have been regarded as having some aromatic character and we were interested in finding out if they behaved in a similar way to the benzyl compounds. In a paper on the mass spectra of 1,3,5-trialkylborazines Powell [3] has suggested that the $(P - R)^+$ ion could have a pseudotropylium ion structure.

In a series of tri-*N*-methylborazines it was observed that the $(M - 1)^+$ ion fragmented by the loss of 1/3 M. The $(M - 1)^+$ could be represented in a pseudobenzyl form (a) or a pseudotropylium form (b) with the loss of 1/3 M being analogous to the loss of C_2H_2 from the tropylium ion.

The Gaussian peak shapes associated with the metastable loss of 1/3 M from the $(M - 1)^+$ source ion were recorded for $(ClBNMe)_3$ (I), $(C_6F_5BNMe)_3$ (II) and $(MeNBCl)_2MeNBMe$ (III). The latter compound could

---

* To whom correspondence should be addressed



(where X = X' = Cl, C_6F_5)
(and X = Cl, X' = Me)

lose 1/3 *M* in two separate processes and both were recorded. The product observed was that which contained a $^{11}B_2$ species. However in cases where chlorine atoms present it was the $^{11}B_2\ ^{35}Cl_2$ product with the product for loss of ClBNMe from III being $^{11}B_2\ ^{35}Cl$.

In the case of compound I the decomposition to the $^{10}B^{11}B^{35}Cl_2$ species was also recorded to demonstrate that all isotopic arrangements gave the same product. Table 1 records the energy releases calculated from the observed peak shapes. These results suggest that the borazines studied undergo an analogous metastable decomposition in the first field free region, as do $C_7H_7^+$ ions generated from benzyl compounds, and that they also form a cyclopentadienyl-type ion by metastable decomposition from their tropylium-like ion. The energy release data shows that the three compounds all underwent a similar decomposition mechanism.

TABLE 1

KINETIC ENERGY RELEASE IN THE 1/3 *M* LOSS FROM $(M-1)^+$ SOURCE ION

Compound	Neutral loss	Product isotope arrangement	T(meV)
$(MeNBCl)_3$	$^{35}Cl^{11}BNMe$	$^{35}Cl_2\ ^{11}B_2$	39
$(MeNBCl)_3$	$^{37}Cl^{11}BNMe$	$^{35}Cl_2\ ^{11}B_2$	38
$(MeNBCl)_3$	$^{35}Cl^{11}BNMe$	$^{35}Cl_2\ ^{11}B^{10}B$	39
$(MeNBCl)_3$	$^{37}Cl^{11}BNMe$	$^{35}Cl_2\ ^{11}B^{10}B$	39
$(C_6F_5BNMe)_3$	C_6F_3BNMe	$^{11}B_2$	44
$(MeNBCl)_2(MeNBMe)$	$^{35}Cl^{11}BNMe$	$^{35}Cl^{11}B_2$	40
$(MeNBCl)_2(MeNBMe)$	$^{37}Cl^{11}BNMe$	$^{35}Cl^{11}B_2$	40
$(MeNBCl)_2(MeNBMe)$	MeBNMe	$^{35}Cl_2\ ^{11}B$	42

If Beynon's [2] results can be used by analogy of like systems then it would appear the tri-*N*-methylborazines have a mixed mechanism. These results provide a further example of the similarities between borazines and aromatic systems.

References

1 K.R. Jennings and T.H. Futnell, J. Chem. Phys., 44 (1966) 4315.
2 R.G. Cooks, J.H. Beynon, M. Bertrand and M.K. Hoffman, Org. Mass. Spec., 7 (1973) 1303.
3 P. Powell, P.J. Sherwood, M. Stephens and E.F.H. Brittain, J. Chem. Soc., A, (1971) 2951.