Notes

Mass Spectrometry in Structural and Stereochemical Problems. CXII.[1] Fragmentation of Two Bicyclic Amines on Electron Impact[2a]

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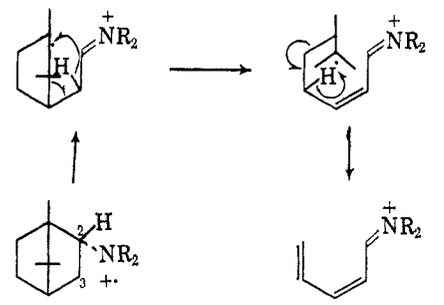
Recently we reported the results of a detailed study of the fragmentation of camphor upon electron impact.[3] Contrary to earlier suggestions in the literature,[4] we found that all of the major peaks in the mass spectrum are due to hydrocarbon species and that accordingly the carbonyl group does not compete effectively with the hydrocarbon framework in directing the fragmentation of this bicyclic molecule.

We have now studied the fragmentation of bornylamine (I) and N,N-dimethylbornylamine (II) in order to determine what effect the more powerful fragmentation-directing amino group[5] has on the fragmentation pattern of this bicyclic system and we report herewith our observations.

Camphor was converted to camphor oxime[6] and the oxime was reduced with sodium and alcohol to a mixture of bornylamine and isobornylamine; pure bornylamine (I) was isolated by the procedure of Hückel[7] and converted to N,N-dimethylbornylamine by Leuckarts' method.[8] N,N-Dimethylbornylamine-2,3,3-d_3 was prepared in a similar manner from camphor-3,3-d_2[3] using the appropriate deuterated reagents. The mass spectra of bornylamine (I) and N,N-dimethylbornylamine (II) were measured under the same conditions as that of camphor[3] and are reproduced in Figures 1 and 2, respectively.

The mass spectrum of bornylamine resembles that of camphor;[3] the base peak is once again at *m/e* 95, and high-resolution measurements indicate that it still represents a hydrocarbon fragment. The peak remains at *m/e* 95 in the spectrum of both II and its 2,3,3-d_3 analog and consequently must be formed by the loss of vinylamine (or N,N-dimethylvinylamine) and a methyl group. Somewhat surprisingly, this peak represents almost the same percentage of the total ion current (Σ_{30}) in the spectra of I and II (10.9 and 11.8%, respectively) as it does in the spectrum[3] of camphor (12.2%) and hence the amino group does not suppress the "directing ability" of the hydrocarbon framework for the formation of this important peak.

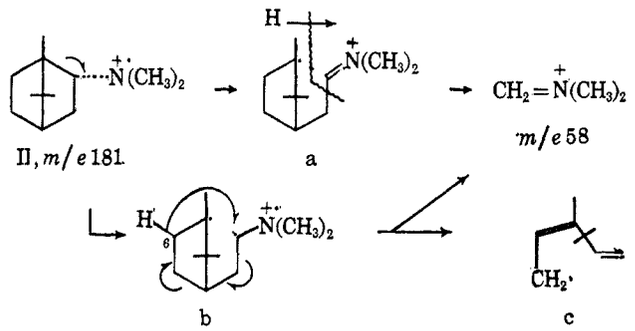
On the other hand, the hydrocarbon fragments found at *m/e* 81, 83, and 109 in the camphor spectrum[3] are very weak in the spectrum (Figure 1) of I and in their place arises an intense peak at *m/e* 82. As demonstrated by high-resolution measurements, this ion has the empirical formula $C_5H_{10}N$ and is shifted to *m/e* 110 in the spectrum (Figure 2) of II and to *m/e* 112 in the spectrum of its 2,3,3-d_3 derivative. Since a strong metastable peak at *m/e* 66.9 in the spectrum (Figure 2) of II indicates that the *m/e* 110 species is formed in one step ($110^2/181 = 66.9$), it is very likely that this ion arises by the same type of amine fragmentation which has been so well documented in the steroid series.[9]



I, R = H, *m/e* 153
II, R = CH_3, *m/e* 181

R = H, *m/e* 82
R = CH_3, *m/e* 110

The base peak in the spectrum (Figure 2) of II appears at *m/e* 58. It corresponds in elemental composition to C_3H_8N (high-resolution measurements) and shifts to *m/e* 59 in the spectrum of the 2,3,3-d_3 analog. The most likely genesis is *via* the α-fission product (a) accompanied by hydrogen transfer. While the source of this hydrogen atom was not established by isotope labeling, the C-6 position is a likely candidate (b → c).



II, *m/e* 181 a *m/e* 58

b c

Another interesting observation is that, although I eliminates ammonia, a methyl group, and ammonia plus a methyl group on electron impact, the dimethylamino analog II loses only a methyl group. A possible

(1) Paper CXI: D. Becher, C. Djerassi, R. E. Moore, H. Singh, and P. J. Scheuer, *J. Org. Chem.*, **31**, 3650 (1966).

(2) (a) We are indebted to the National Institutes of Health for financial assistance (Grant No. GM-06840); (b) National Institutes of Health Postdoctoral Fellow, 1964–1965.

(3) D. S. Weinberg and C. Djerassi, *J. Org. Chem.*, **31**, 115 (1966).

(4) (a) R. I. Reed, "Ion Production by Electron Impact," Academic Press Inc., New York, N. Y., 1962, pp 204–206; (b) "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, Chapter 13.

(5) For leading references, see H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Structure Elucidation of Natural Products by Mass Spectrometry," Vol. 2, Holden-Day, Inc., San Francisco, Calif., 1964, Chapter 18.

(6) K. Auwers, *Ber.*, **22**, 605 (1922).

(7) W. Hückel and P. Rieckmann, *Ann.*, **625**, 1 (1959).

(8) M. L. Moore, *Org. Reactions*, **5**, 301 (1949).

(9) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Vol. 1, Holden-Day, Inc., San Francisco, Calif., 1964, p 76.

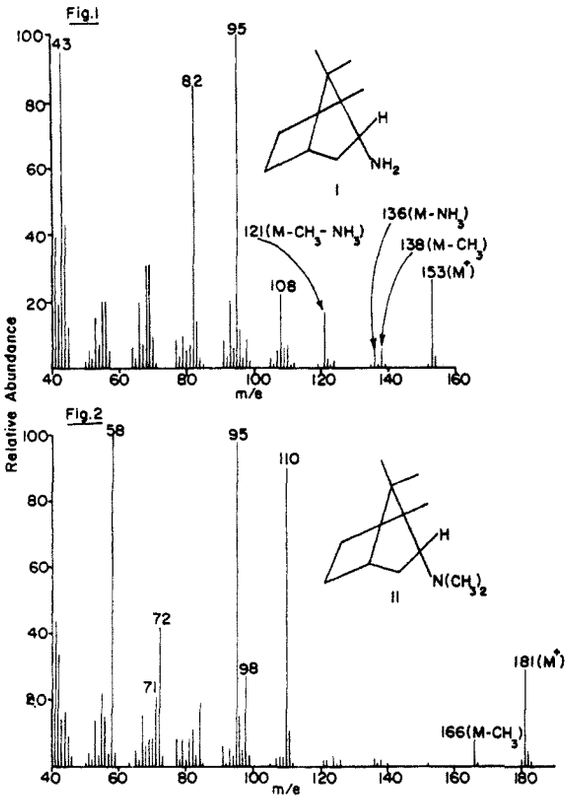


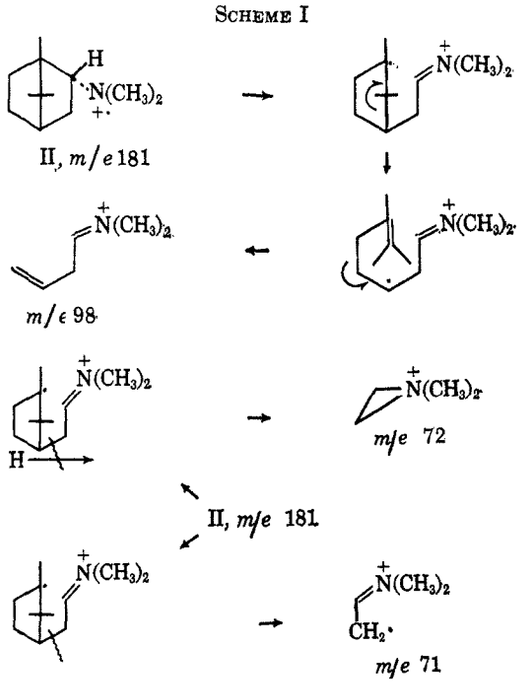
Figure 1.—Mass spectrum of bornylamine (I).
Figure 2.—Mass spectrum of N,N-dimethylbornylamine (II).

explanation may be the greater bulk of the dimethylamino group which interferes with the abstraction of a hydrogen atom.

The remaining peaks of interest in the spectrum (Figure 2) of II are found at *m/e* 71, 72, and 98. These ions have the empirical formulas C_4H_9N, $C_4H_{10}N$, and $C_6H_{12}N$, respectively, and probably arise in the manner shown in Scheme I.

These postulates are fully supported by the deuterium shifts observed in the spectrum of N,N-dimethylamino-bornylamine-2,3,3-d_3: *m/e* 98 shifts to *m/e* 101, *m/e* 72 to *m/e* 75, and *m/e* 71 to *m/e* 74.

SCHEME I



In conclusion, it is interesting to note that in this bicyclic system the hydrocarbon framework has such a powerful fragmentation-directing ability that it can compete effectively with the otherwise very strong fragmentation-directing dimethylamine function. As a consequence, in contrast to the usual observation[5] that dimethylamino substituents lead to a simplification of a given mass spectrum, a more complicated spectrum ensues in such highly fused systems. These observations further substantiate the earlier[3] conclusion that the *a priori* prediction of the mass spectral fragmentation of bicyclic monoterpenes is fraught with danger.

Fluorination of Tetrabromo-2,3-diaza-1,3-butadiene

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The preparation and characterization of tetrafluoro-2,3-diaza-1,3-butadiene (CF_2=N—N=CF_2) from the pyrolysis of difluorodiazirine have been reported.[1] We have investigated some of the chemical, physical, and spectral properties of the material obtained from CF_2N_2, and find that they differ from those which have been reported by Schroeder and co-workers[2] from the silver(I) fluoride fluorination of tetrabromo-2,3-diaza-1,3-butadiene (carbonyl bromide azine) or 2,5-dibromo-1,3,4-thiadiazole. In order to obtain further information bearing on this apparent discrepancy, we have examined the fluorination of CBr_2=N—N=CBr_2 with both AgF and AgF_2.

Tetrabromo-2,3-diaza-1,3-butadiene was prepared according to Thiele[3] by the acidic stannous chloride reduction of sodium azotetrazole, followed by bromination without isolation of intermediates. This material, after recrystallization from butyl chloride, was used in the fluorination studies.

The reaction of silver(II) fluoride (AgF_2) with tetrabromo-2,3-diaza-1,3-butadiene is rapid. Thus, when a mixture of the two solids is allowed to warm from 0° to room temperature, the reaction is explosive in nature with extremely vigorous gas evolution. The crude volatile product is a mixture of fluorinated azo derivatives, such as CF_3—N=N—CF_2Br, CF_3—N=N—CF_3, and CF_3—N=N—$CFBr_2$ (in order of decreasing yield). Small quantities of monochloroazo compounds are also isolated owing to the presence of chlorinated impurities (see the Experimental Section). The vigorous nature of this reaction, as well as the mixture of products, implies limited utility as a synthesis technique.

On the other hand, AgF_2 converts tetrabromo-2,3-diaza-1,3-butadiene to hexafluoroazomethane (CF_3—

(1) R. A. Mitsch, *J. Heterocyclic Chem.*, **1**, 59 (1964).
(2) H. Schroeder, R. Rätz, W. Schnabel, H. Ulrich, E. Kober, and C. Grundmann, *J. Org. Chem.*, **27**, 2589 (1962).
(3) J. Thiele, *Ann.*, **303**, 57, 70 (1898).