

THE MASS SPECTRA OF SCHIFF BASES

II.* TWO DEUTERATED SPECIES

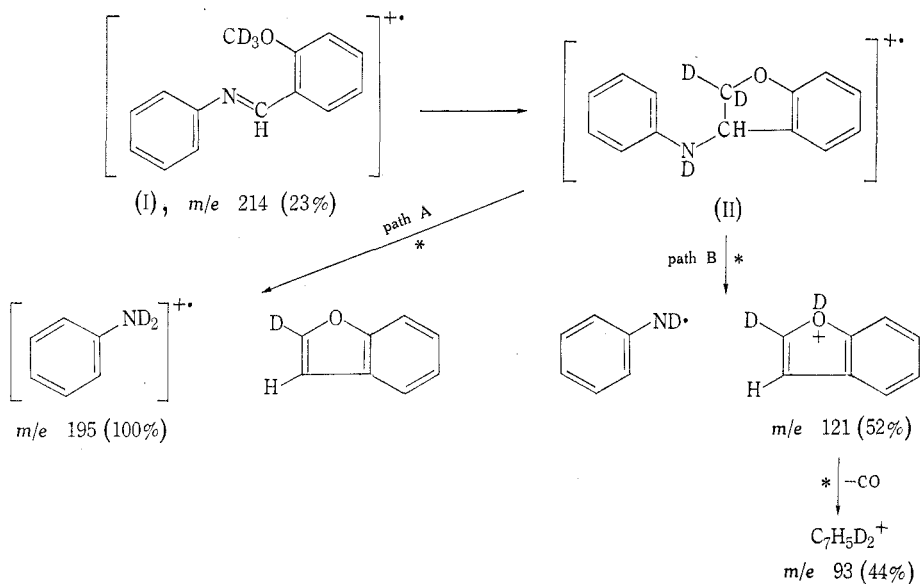
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The behaviour of a series of Schiff bases under electron impact has been described.¹ As an extension of that work, results obtained with *o*-trideuteromethoxybenzylideneaniline and α -deuterobenzylideneaniline are now reported.

o-Trideuteromethoxybenzylideneaniline (I)

Anils derived from *o*-anisaldehyde have as the base peak in their mass spectrum the ion corresponding to the amine.¹ This requires a rearrangement in which two hydrogens are transferred to the nitrogen. A mechanism was proposed in which both hydrogens originated in the methoxy group and we have examined the mass spectrum of trideuteromethoxybenzylideneaniline to check this hypothesis.



Scheme 1

In the mass spectrum of (I), the base peak is shifted to m/e 95 corresponding to $C_6H_5ND_2$, and the intense peak previously seen at m/e 119 is now found at m/e 121.

* Part I, *Aust. J. Chem.*, 1966, **19**, 251.

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¹ Elias, D. J., and Gillis, R. G., *Aust. J. Chem.*, 1966, **19**, 251.

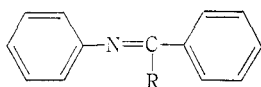
This confirms the suggested mechanism (Scheme 1), which required transfer of a deuteron from the methoxy group to the nitrogen followed by joining of the azomethine and methoxy carbon atoms giving (II).

The rearranged molecular ion (II) can then decompose by path A with transfer of a second deuterium to the nitrogen atom and nitrogen-carbon fission giving m/e 95, or by path B with simple nitrogen-carbon fission giving m/e 121 which can be represented as the deuterated benzofuran. Both paths are confirmed by metastable ions, m^*/e $42 \cdot 2 \equiv 214 \rightarrow 95$ and m^*/e $68 \cdot 4 \equiv 214 \rightarrow 121$. As before, the ion m/e 121 loses carbon monoxide giving m/e 93 (m^*/e 71.5).

α -Deuterobenzylideneaniline (IIIa)

Only indirect evidence has been available for the assignment of the $(M-1)^+$ peak in the mass spectrum of Schiff bases to the loss of the azomethine hydrogen. Elias and Gillis based their conclusion on the comparison of azobenzene, benzylideneaniline, and stilbene;¹ Bowie and co-workers² on the spectra of ring-deuterated benzylideneanilines.

In the 70-eV mass spectrum of (IIIa) prepared from α -deuterobenzaldehyde, a metastable ion can be seen for the loss of deuterium, m^*/e 178 \equiv 182 \rightarrow 180. The



(IIIa) R = D, m/e 182

(IIIb) R = H, m/e 181

relative intensities of m/e 182, 181, and 180 are 100 : 28 : 85. Hence in (IIIb), ring hydrogen atoms are lost as well as the azomethine hydrogen in the approximate ratio 1 : 3. If the loss of ring hydrogen atoms is random, then benzylideneaniline tri-deuterated in either ring should show $(M-D)^+$ 3/10 of 28, and $(M-H)^+$ 7/10 of 28 plus 85 relative to $M = 100$, that is, the relative intensities of m/e 184, 183, and 182 should be 100 : 105 : 8. This calculation agrees with the experimental results of Bowie *et al.*,² but their deduction that "the hydrogen lost in the $M-H$ decomposition comes almost exclusively ($> 90\%$) from the azomethine moiety" is invalid. It also follows from our results that data obtained at 70 eV cannot be used for relating the intensity of the $(M-1)^+$ ion to substituent effects.

Experimental

Salicylideneaniline was trideuteromethylated with CD_3I (Stohler) and NaOH in dimethyl sulphoxide.³ The product had d_3 , 98%. The principal peaks above m/e 90 in the mass spectrum were, m/e (intensity): 214(23), 181(6), 167(6), 121(52), 119(7), 96(8), 95(100), 94(8), 93(44). α -Deuterobenzaldehyde was prepared by exchanging benzylidene-1,1'-dipyridinium dibromide with D_2O twice;⁴ the mixture was hydrolysed, the aldehyde was extracted with ether and treated with aniline in the usual manner. The benzylideneaniline so obtained had d_1 , 97%; n.m.r. intensity measurements showed that there was less than 3% hydrogen in the azomethine moiety.

Mass spectra were determined in an Atlas CH4 instrument; metastable ions were observed with a 4-decade logarithmic transfer recorder designed and constructed by Dr J. Ternan.

² Bowie, J. H., Cooks, R. G., Fisher, J. W., and Spotswood, T. McL., *Aust. J. Chem.*, 1968, **21**, 2021.

³ Gillis, R. G., *Tetrahedron Lett.*, 1968, 1413.

⁴ Olofson, R. A., and Zimmerman, D. M., *J. Am. chem. Soc.*, 1967, **89**, 5057.