Aryl Migration under Electron Impact Conditions

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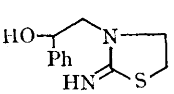
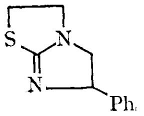
MUCH attention has been paid recently to the McLafferty hydrogen rearrangements,[1] to the possibility of similar alkyl and aryl rearrangements[2] and in more general terms to a number of cases involving the formation of fresh C–C and/or C–O bonds.[3] There being such interest apparent, it is felt that attention should be drawn to an example involving what seems to be the aryl counterpart of the McLafferty hydrogen rearrangement.

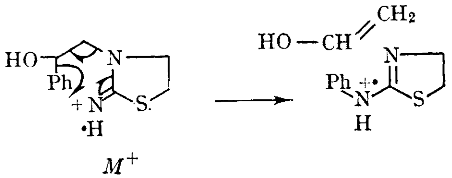


(I)



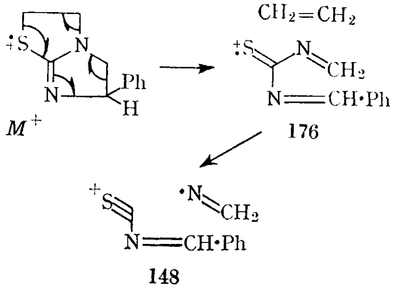
(II)

While examining the mass spectra of 3-(β-hydroxy-β-phenylethyl)-2-iminothiazolidine (I) and a related compound 6-phenyl-2,3,5,6-tetrahydroimidazo[2,1-*b*]thiazole (II), strong fragment peaks, whose existence seemed unlikely on the basis of the original structures, were encountered. In the case of compound (I) (M^+,*m/e* 222) an abundant fragment at *m/e* 178 (4·0% of base peak) was formed from the molecular ion (m^* 142·7). Accurate mass measurement[4] showed this fragment to have the composition $C_9H_{10}N_2S$, *i.e.*, a loss of C_2H_4O. The most straightforward way to obtain this loss would appear to be as illustrated below, *viz.*, a McLafferty type rearrangement of a phenyl group.



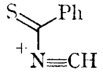
A doublet occurs at *m/e* 103 (22% of base peak, having the compositions $C_3H_7N_2S$ and C_8H_7 (respective abundances 3 : 1). The former would appear to be the protonated form of the normal McLafferty hydrogen rearrangement. A peak at *m/e* 107 (C_7H_7O; 6·0% of base peak) shows the original association of phenyl and oxygen while a small peak at *m/e* 93 (C_6H_7N; 0·15% of base) shows a connection to a lesser extent of the aromatic ring and a nitrogen atom.

The main fragmentation path of compound (II) consists of the loss of ethylene to *m/e* 176 (m^* 151·8) followed by a further loss of 28 (m^* 124·5) to the base peak at *m/e* 148, C_8H_6NS. At *m/e* 121 is a peak (41% of the base peak) which mass measurement shows to be C_7H_5S, in other words C_6H_5–$C{\equiv}S^+$. The origin of this fragment is quite obscure until on careful examination of the spectrum one finds a small metastable peak at *m/e* 99·0 indicating a fragmentation from *m/e* 148 to 121. The fragmentation path to 148 can be represented thus:



To obtain C_6H_5CS from *m/e* 148 one must invoke either a phenyl transfer to (III) or a four-membered-ring intermediate involving the sulphur. Of these two the former seems far more feasible, the latter involving further hydrogen transfers to get the required products whereas (III) can readily give $PhC{\equiv}S^+$ plus a molecule of hydrogen cyanide.

Further details of the spectra of these and related compounds including specifically deuterium-labelled compounds will be reported shortly.



(III)

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[1] C. Djerassi, M. Fischer, and J. B. Thomson, *Chem. Comm.*, 1966, 12.

[2] R. R. Arndt and C. Djerassi, *Chem. Comm.*, 1965, 578.

[3] J. H. Bowie, R. Grigg, D. H. Williams, S.-O. Lawesson, and G. Schroll, *Chem. Comm.*, 1965, 403.

[4] All spectra and mass measurements were obtained on an A.E.I. MS.9 mass spectrometer.