Mass Spectrometry in Structural and Stereochemical Problems. Absence of Electron-impact induced Methyl Migration in 2,2,8,8-Tetramethylnonan-5-one

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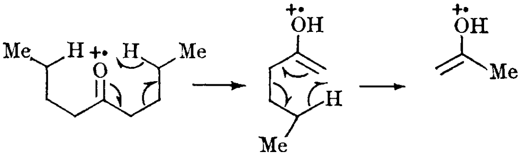
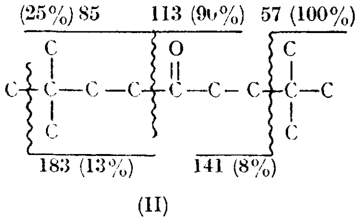
HYDROGEN migrations caused by electron impact have been studied widely and are of major importance in the interpretation of mass-spectral fragmentation mechanisms.[1] Of equal mechanistic significance is a knowledge of alkyl and aryl migrations,[2–4] so that it may become possible to predict when rearrangements are likely to occur. In that connection, one of the key questions that needs to be answered is whether alkyl migrations will replace hydrogen migrations when alkyl groups completely replace all relevant hydrogens in a compound where electron-impact induced hydrogen transfer has been demonstrated.

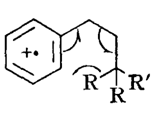
The most widely studied hydrogen migration in mass spectrometry is the McLafferty rearrangement,[5] which in suitable ketones such as dibutyl ketone (I) can occur twice [(I) → *a* → *b*] by transfer of a γ-hydrogen atom as shown by appropriate deuterium labelling.[5b] It was of considerable interest, therefore, to determine whether single [analogous to (I) → *a*] or double (analogous to *a* → *b*) methyl migration would occur in 2,2,8,8-tetramethylnonan-5-one (II), a ketone in which all six γ-hydrogen atoms of (I) are replaced by methyl groups. This hitherto unknown ketone was prepared by a Grignard reaction using 1-bromo-3,3-dimethylbutane[6] and ethyl formate



(I) *a* (*m*/*e* 100) *b* (*m*/*e* 58)



(II)



(III)

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[1] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds", Holden-Day, San Francisco, 1964.

[2] M. Fischer and C. Djerassi, *Chem. Ber.*, in the press and references cited therein.

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

[5] (a) F. W. McLafferty, *Analyt. Chem.*, 1959, **31**, 82; (b) H. Budzikiewicz, C. Fenselaw, and C. Djerassi, *Tetrahedron*, in the press.

[6] L. Schmerling, *J. Amer. Chem. Soc.*, 1945, **67**, 1152, and references cited therein.

followed by Jones oxidation[7] and gas-chromatographic purification (semicarbazone, m.p. 119—120°; oxime, m.p. 80—81°).

The principal mass-spectral fragments are indicated in formula (II) and the assignments are confirmed by the appropriate peak shifts encountered in the mass spectrum of the $\alpha\alpha\alpha'\alpha'$-[$^2H_4$]-analogue of (II), which was prepared by direct acid-catalysed exchange on a gas-chromatography column.[8] Negligible peaks (other than ^{13}C contributions from *m/e* 141 and *m/e* 85) were observed at *m/e* 142 or *m/e* 86 which would correspond to methyl migrations analogous to a single [(I) → *a*] or double (*a* → *b*) McLafferty rearrangement.

Similarly, it has been shown[2] recently by deuterium labelling that 3,3-dimethylbutylbenzene (III, $R = R' = Me$) does not undergo any methyl migration in marked contrast to the well documented[9] hydrogen transfer [see arrows in (III, $R = H$, $R' = Me$)] in butylbenzene. One may conclude from our results that at the present time analogies between mass-spectrometric hydrogen and methyl migrations are not justified and that the latter must be studied and evaluated mechanistically on their own merits.

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[7] K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 1946, 39.

[8] See: W. J. Richter, M. Senn and A. L. Burlingame, *Tetrahedron Letters*, 1965, 1235.

[9] J. D. McCollum and S. Meyerson, *J. Amer. Chem. Soc.*, 1959, **81**, 4116.