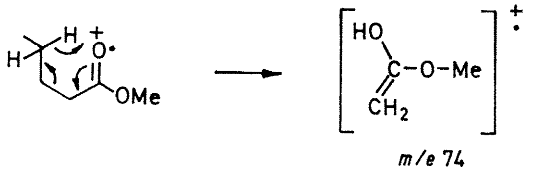
Specificity of Hydrogen Rearrangement in Phenyl Valerate Fragmentation Upon Electron Impact

By GRANT G SMITH* and SCOTT W COWLEY
(*Department of Chemistry, Utah State University, Logan, Utah* 84321)

Summary Hydrogen rearrangement in phenyl valerate upon electron impact was found to be site selective (87%) from the α-position

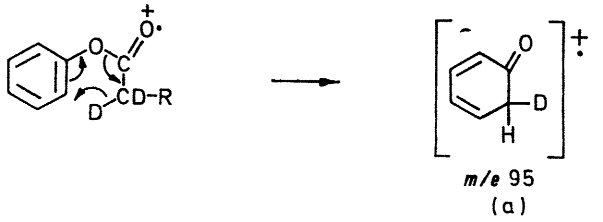
STRAIGHT-CHAIN methyl esters readily undergo hydrogen-transfer due to a McLafferty rearrangement upon electron impact (Scheme 1) [1]



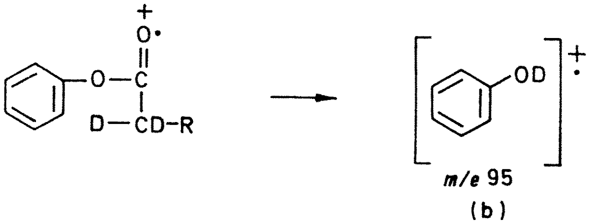
SCHEME 1 *McLafferty rearrangement in methylalkanoates* Specificity of γ-H transfer >95%

The mass spectrum of straight-chain phenyl esters such as phenyl valerate and phenyl butanoate[2] were studied However, no corresponding peak of any significance was observed at *m/e* 152, which would have resulted from a similar hydrogen rearrangement as that in Scheme 1 A hydrogen rearrangement does occur but involves the phenolic portion of the molecule, instead, producing a base peak at *m/e* 94

Deuterium labelling of the phenyl valerate in the α-position (essentially 100%) indicated that 87% of hydrogen transfer was from the α-position and only 13% resulted from hydrogen abstraction from other positions in the chain Either a six-membered hydrogen rearrangement involving the phenyl ring (Scheme 2) or a four-membered cyclic hydrogen transfer may be involved (Scheme 3)



SCHEME 2 *Six-membered transition state* Specificity of γ-H transfer = 87%



SCHEME 3 *Four-membered transition state*

Various aromatic compounds undergo hydrogen transfer upon electron impact Deuterium labelling has demonstrated that such compounds as alkylbenzenes[3] and the corresponding alcohols[4] and ethers[4,5] (with the oxygen in the 2′-, 3′-, or 4′-position), all undergo hydrogen transfer from the 3′-position This supports the mechanism shown in the Scheme 2 However, other studies using deuterium labelling have shown that n-butyl phenyl ether (with the oxygen atom in the 1′-position), exhibits a *m/e* 95 peak resulting from a random hydrogen abstraction from the alkyl chain. Based on the rationale used by MacLeod and Djerassi[6] a cyclic four-membered rearrangement (Scheme 3) is also a logical fragmentation pattern.

Phenol exhibits a base peak at *m/e* 94, and upon fragmentation produces two characteristic peaks at *m/e* 66 and 65, resulting from a loss of CO and CHO, respectively.[7] It has been suggested that phenol passes through a cyclohexadienone intermediate similar to (a) in Scheme 2 to produce the cyclopentadiene ion at *m/e* 66.[8]

Rinehart and Siegel[9] and Woodgate and Djerassi[10] have shown that there is no loss of ring carbon identity in the molecular ion of phenol (using [1-^{13}C]phenol) prior to expulsion of CO. Likewise, Woodgate and Djerassi showed that scrambling did not occur with the carbon in the ring during the fragmentation of n-butyl [1-^{13}C]phenyl ether to the fragment *m/e* 94 and subsequently to *m/e* 66 by loss of CO. They concluded that the ether formed a phenol-like ion at *m/e* 94.

Comparison of the two spectra of phenyl valerate with that of phenol shows that the loss of CO from the phenol-like ion at *m/e* 94 resulting from hydrogen migration fragmentation from the molecular ion of the ester is not as ready as from phenol itself. This indicates that either the structures for the two ions at *m/e* 94 differ and/or that they have significantly different energy states.

We thank the National Science Foundation for financial support and Dr. A. Duffield for discussions.

(*Received, July 12th*, 1971; *Com.* 711.)

---

[1] R. Ryhage and E. Stenhagen, *Arkiv Kemi*, 1959, **13**, 523; W. Sonneveld, *Rec. Trav. chim.*, 1965, **84**, 45; T. M. Trent, F. D. Miller, and G. H. Brown, *Appl. Spectroscopy*, 1961, **15**, 64.

[2] F. W. McLafferty and T. Wachs, unpublished results.

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

[4] J. K. MacLeod and C. Djerassi, *Tetrahedron Letters*, 1966, 2183.

[5] J. A. Gilpin, *J. Chem. Phys.*, 1958, **28**, 521; J. D. McCollum and S. Meyerson, unpublished results quoted in "Mass Spectrometry, of Organic Ions", Ed. F. W. McLafferty, Academic Press, New York, 1963, p. 510.

[6] J. K. MacLeod and C. Djerassi, *J. Amer. Chem. Soc.*, 1966, **88**, 1840.

[7] T. Aczel and H. E. Lumpkin, *Analyt. Chem.*, 1960, **32**, 1819; J. H. Beynon, "Mass Spectrometry and its Application to Organic Chemistry," Elsevier, Amsterdam, 1960, p. 352; J. Momigny, *Bull. Soc. roy. Sci. Liege*, 1953, **22**, 541.

[8] J. H. Beynon, G. R. Lester, and A. E. Williams, *J. Phys. Chem.*, 1959, **63**, 1861.

[9] K. L. Rinehart, Jr. and A. Siegel, American Chemical Society meetings, New York, September, 1969, abstract 66.

[10] P. D. Woodgate and C. Djerassi, *Org. Mass Spectrometry*, 1970, **3**, 1093.