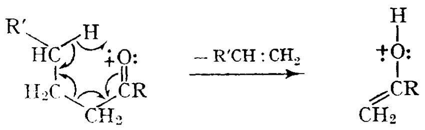
Suppression of McLafferty Rearrangement in the Mass Spectrometric Fragmentation of Even-electron Systems

By MANFRED KRAFT and G. SPITELLER*

(*Department of Organic Chemistry, University of Göttingen, Germany*)

RECENTLY it was suggested that the prerequisite for the occurrence of a McLafferty rearrangement[1], (I) ⟶ (a), is the presence of an odd-electron species of type (I):[2,3]



(I) (a)

We now present evidence that this conclusion cannot be generalized. Disubstituted malonic acids of type (II) do not show molecular ions in their mass spectra, because they easily undergo a McLafferty rearrangement to form the ion radical (b), which is cleaved as indicated to form (c). This fragment is an even-electron species, but even so it is further cleaved in the course of a second McLafferty rearrangement to an ion of mass 87 (d).

The molecular formula of (d) was established by high resolution.† A final proof for the reaction (c) → (d) was provided by the spectrum of the tetradeuterated compound (III), in which the peak

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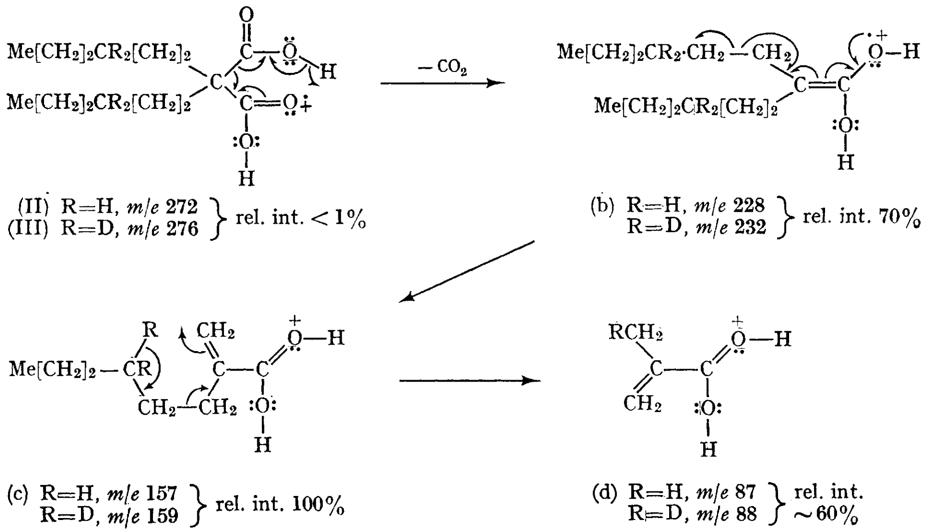
† We thank Dr. W. Vetter for this measurement, performed on MS 9 double focussing instrument.



(II) R=H, m/e 272
(III) R=D, m/e 276 } rel. int. < 1%

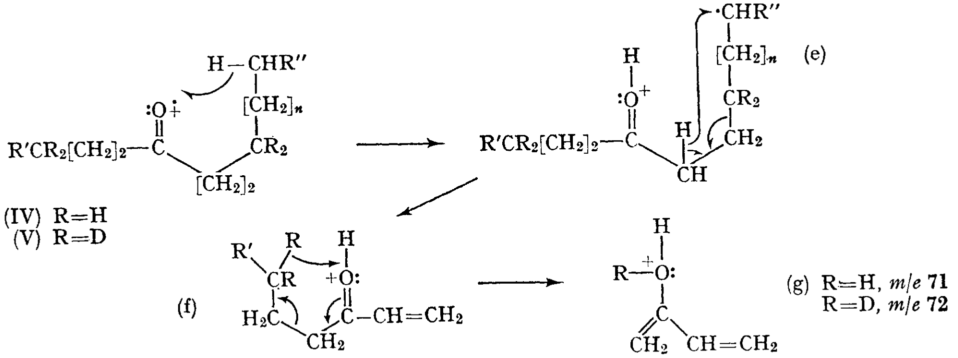
(b) R=H, m/e 228
R=D, m/e 232 } rel. int. 70%

(c) R=H, m/e 157
R=D, m/e 159 } rel. int. 100%

(d) R=H, m/e 87
R=D, m/e 88 } rel. int. ~60%

of mass 157 shifted to mass 159 and that of mass 87 to mass 88.

A further example are the spectra of straight-chain aliphatic ketones. Aliphatic ketones of type (IV) lose in a nonspecific double hydrogen rearrangement[4] (proved by labelling experiments[5]) a radical to form the even-electron species (f), (e) ⟶ (f).



(IV) R=H
(V) R=D

(e)

(f)

(g) R=H, m/e 71
R=D, m/e 72

This fragment (f) is further degraded by a McLafferty rearrangement, which we proved with the compound deuterated in γ-position (V). The elemental composition of (g) was again established by high resolution†.

These examples show that the prerequisite for a McLafferty rearrangement is not an odd-electron species of type (I) as we stated earlier,[6] but the possibility of developing a suitable transition state. The hydrogen rearrangement may occur either as a proton shift (c) ⟶ (d) or as a shift of a hydrogen atom (I) ⟶ (a) or even as a shift of a hydrid ion (f) ⟶ (g).

This independence from a charge or a radical site is unique; nearly all other decomposition reactions (another exception is the retro-Diels–Alder reaction) are determined by the position of the charge or the radical site.

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[6] G. Spiteller and M. Spiteller-Friedmann, *Monatsh.*, 1964, **95**, 257.