Localization of Acetylenic Bonds by Mass Spectrometry*

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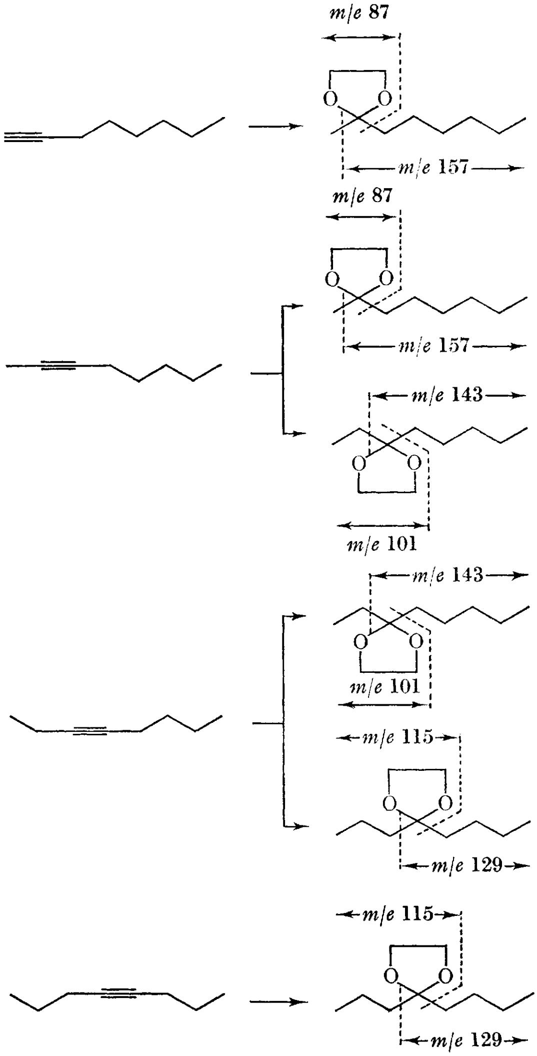
IT is difficult to localize ethylenic or acetylenic bonds in an aliphatic chain by mass spectrometry. In the case of ethylenic compounds, this can, however, be achieved when various functional groups are introduced in the position of the previous unsaturation.[1] In continuation of our earlier work on the orientation of fragmentation in mass spectrometry by introduction of functional groups, we report a simple method for localizing triple bonds in a given skeleton.

Acetylenic compounds, heated with ethylene glycol and a trace of Hennion's catalyst,[2] give one or two ethylene ketals, depending upon the structure of the compound. The crude mixture, separated from tars by g.l.c., is introduced into the mass spectrometer. As described previously,[3] a very intense fragmentation takes place α to the functional group, which outweighs any other fragmentation process. For instance, oct-1-yne, oct-2-yne, oct-3-yne, and oct-4-yne can easily be distinguished, as shown in Scheme 1.

The same applies to acetylenic fatty esters, *e.g.*, methyl stearolate, which gives a mixture of two ketals and therefore four intense peaks. In the latter case, there is in addition, as expected, an *m/e* 74 peak, due to McLafferty's fragmentation.



Scheme 1

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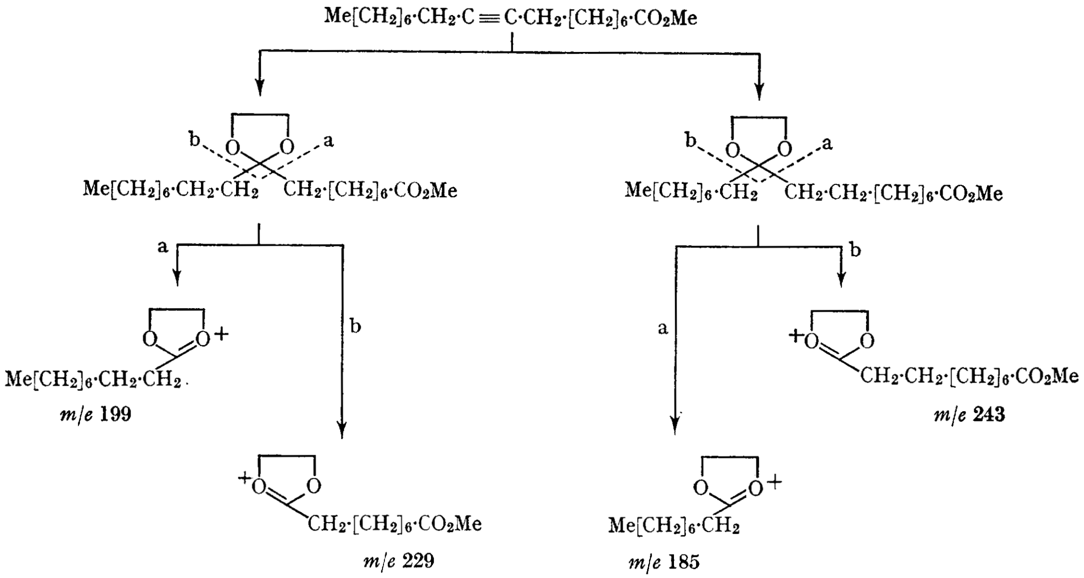
* Part VIII in the series, Orientation of fragmentation in mass spectrometry by introduction of functional groups; Part VII, H. E. Audier, M. Fétizon, and J. C. Gramain, *Bull. Soc. chim. France*, 1965, 3088.

[1] K. Biemann, "Mass Spectrometry," McGraw Hill, New York, 1962; H. E. Audier, S. Bory, M. Fétizon, P. Longevialle, R. Toubiana, *Bull. Soc. chim. France*, 1964 3034; N. Dinh Nguyen and R. Rhage, *J. Res. Inst. Catalysis Hokkaido Univ.*, 1960, **8**, 73; N. Dinh Nguyen, R. Ryhage, and S. Ställberg-Stenhagen; *Arkiv. Kemi.*, 1960, **15**, 433; J. A. McCloskey and M. J. McClelland, *J. Amer. Chem. Soc.*, 1965, **87**, 5090; R. E. Wolff, G. Wolff, and J. A. McCloskey, *Tetrahedron*, 1966, **22**, 3093.



Scheme 2

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[2] G. F. Hennion, O. B. Killian, T. H. Wugh, and J. A. Niewland, *J. Amer. Chem. Soc.*, 1934, **56**, 1130.

[3] M. Fétizon, H. E. Audier, J. C. Gramain, J. Schalbar, and B. Waegell, *Bull. Soc. chim. France*, 1964, 1880.