SPECIALIA

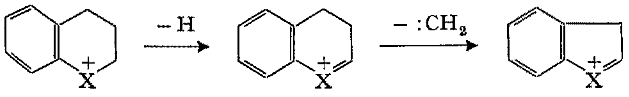
Electron Impact Studies IV. Expulsion of Methylene Under Electron Impact

Ring expansion and contraction under electron impact are well documented in the literature[1,2]. The classical work of Meyerson et al.[1] showed that the tropylium ion is formed by the ring expansion of the benzene ring leading to the insertion of a methylene group. Similar ring expansions have been postulated for the furfuryl and thenyl ions formed by fragmentation of alkylfurans[3] and alkyl thiophenes[4].

Ring contraction by the expulsion of carbon monoxide has been reported by Beynon etal.[5] in the fragmentation of cyclic ketones and quinones. Willhalm et al.[2] proposed the expulsion of methylene to explain the formation of the fragment with m/e 119 from the M-1 species in the mass spectral fragmentation of chroman. They observed a metastable peak corresponding to this rearrangement. No labelling experiments were carried out.

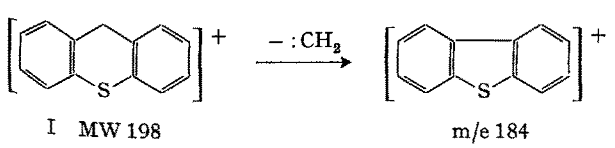
The expulsion of a methylene is a very rare process in mass spectrometry. Recently we have initiated work on the electron impact fragmentation of some sulphur compounds. In the course of this investigation we have observed fragmentation modes involving the extrusion of a methylene under electron impact.

An analysis of the mass spectra of tetralin and thiochroman showed that the molecular ion readily loses 1 hydrogen atom. The M-1 species then loses methylene to give very stable ions at m/e 117 (24%) and m/e 135 (29%) in the fragmentation of tetralin and thiachroman respectively. The following mechanism is proposed to explain the expulsion of a methylene from the M-1 species under electron impact.

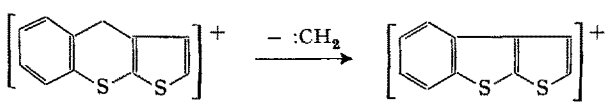


X = CH$_2$, S or O

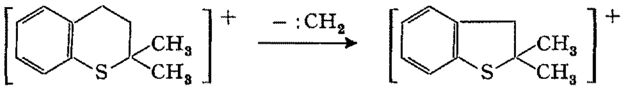
This observation led us to examine the mass spectra of a few sulphur compounds in which we expected the loss of a methylene from the molecular ion. The mass spectra of thioxanthene (I), thieno-(2,3-b)-benzothiopyran (II) and 2,2-dimethylthiachroman (III) were recorded. The loss of a hydrogen atom from the molecular ion is found to be very significant. The peaks observed at m/e 184 (62%), m/e 190 (50%) and m/e 164 (40%) in the spectra of I, II and III respectively can only be explained by assuming the expulsion of methylene from the molecular ion. A comparison of the mass spectra of II and IV[6] showed great similarity which indicates that in the fragmentation of II, IV is a probable intermediate.



I MW 198 m/e 184



II MW 204 IV m/e 190



III MW 178 m/e 164

The dideuterated analogues of compounds I and II were prepared from the corresponding ketones by Clemmensen reduction using zinc amalgam and deuterated hydrochloric acid[7]. In the mass spectra of these dideuterated compounds peaks were observed corresponding to the loss of dideuterated methylene (:CD$_2$) from the molecular ion. This observation supports the proposed fragmentation mode which involves the expulsion of a methylene. Metastable peaks were also recorded which further supports the above observations. In the mass spectra of 2,2-dimethylthiachroman, peaks are observed which correspond to the loss of a methylene from fragment ions; e.g. m/e 162 $^{-}$:CH$_2$ m/e 148 (fragment with mass 162 is formed by the loss of 16 mass units (M-CH$_4$) from the molecular ion of (III)).

The expulsion of methylene appears to resemble the expulsion of carbon monoxide from cyclic ketones and quinones. The driving force for this fragmentation mode seems to be the stability of the fragment formed as a result of the loss of a methylene. This break-down pattern is therefore likely to operate only in specific aromatic systems of the type illustrated above where the fragment left after loss of methylene is stable[8].

Zusammenfassung. Es wird gezeigt, dass bei geeigneten Verbindungen die Ausstossung der Methylengruppe im Massenspektrum eine bevorzugte Reaktionsweise darstellt. Diese Reaktionsweise gleicht derjenigen der Abgabe von Kohlenmonoxyd aus cyclischen Ketonen oder Chinonen.

B. D. Tilak, K. G. Das and H. M. El-Namaky

National Chemical Laboratory, Poona 8 (India),
6th March 1967.

---

[1] H. M. Grubb and S. Meyerson, in *Mass Spectrometry of Organic ions* (Ed. F. W. McLafferty; Academic Press, Inc., New York 1963), p. 493.

[2] B. Willhalm, A. F. Thomas and F. Gautschi, Tetrahedron *20*, 1185 (1964).

[3] J. Collin, Bull. Soc. chim. Belg. *69*, 575 (1960).

[4] V. Hanus and V. Cermak, Colln Czech. chem. Commun. Engl. Edn *24*, 1602 (1959).

[5] J. H. Beynon and A. E. Williams, Appl. Spectrosc. *14*, 156 (1960).

[6] R. B. Mitra, L. J. Pandya and B. D. Tilak, J. scient. ind. Res. *16B*, 348 (1957).

[7] O. Dann, G. Volz and O. Huber, Justus Liebigs Annln Chem. *587*, 16 (1954).

[8] NCL communication No. 1021.