

“Metastable Peaks” for Two-step Fragmentations

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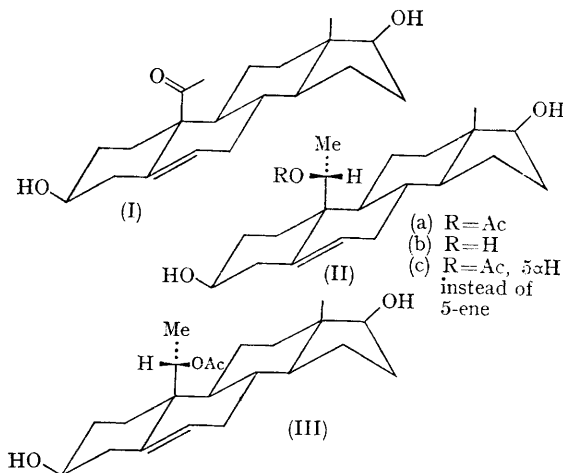
THE occurrence of “metastable peaks” attributable to an apparent one-step loss of two carbon monoxides from the molecular ions of certain substituted cyclobutane-1,3-diones has been reported.¹ Similar metastable transitions have been observed in the mass spectra of organometallic compounds containing more than one metal atom.²

More recently “metastable peaks” were reported³ for what could be considered a one-step loss of

CO₂H from ions, in which the two oxygen atoms were separated by four carbon atoms. It was suggested that the metastable transition was related to a “double fragmentation”, *i.e.*, loss of CO and OH particles. An alternative process whereby a CO₂H group was lost as a single entity was also considered, but such a loss should be preceded by a drastic rearrangement.³ A fragmentation involving the loss of two or more

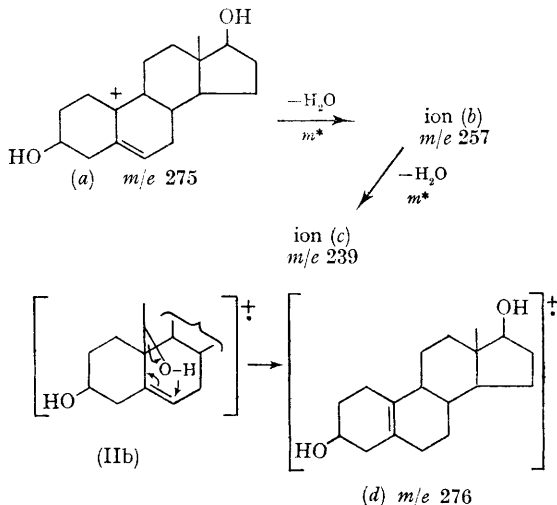
neutral particles in consecutive decomposition reactions was suggested by Jennings,⁴ for reactions in which the postulated neutral fragment is not a well-known stable radical or molecule. Even though a metastable transition corresponding to the loss of a relatively large fragment could be detected, a stepwise sequence was preferred.⁴ This phenomenon may occur if a metastable ion loses a neutral fragment in a slow process and is followed in a much shorter time by the ejection of a further neutral fragment. The "metastable peak" will then indicate that both fragments have been effectively lost together.

Here we report the detection of metastable transitions, resulting from an apparent one-step loss of two molecules of H₂O. During studies on steroidal neopentyl systems, 19(*R*)-acetoxy-19a-methyl-3 β ,17 β -dihydroxyandrost-5-ene (IIa) and 19(*S*)-acetoxy-19a-methyl-3 β ,17 β -dihydroxyandrost-5-ene (III) were prepared.⁵ The products were tentatively assigned the (*R*)- and (*S*)-configurations on the basis of their ability or otherwise to form a 3,19-oxide with the respective 3-ketones of the A/B *trans*-series. The alcohol which gave the 3 α -methoxy-3 β ,19-oxide under standard conditions of exposure to methanol and toluene-*p*-sulphonic acid at ambient temperature was assigned the 19(*R*)-configuration. The alcohol which resisted the conversion into the oxido-ether under these conditions was considered to have the 19(*S*)-configuration. The 19-ketone (I) was prepared from both alcohols.



A characteristic feature of fragmentation of ketone (I) and the acetoxy-derivatives 19(*R*)-(IIa)

and 19(*S*)-(III) under electron impact was the appearance in the high mass region of the spectra (above m/e 100) of three important peaks at m/e 275, 257, and 239.[†] Obviously the m/e 275 ion (*a*) is formed by the cleavage of 10-19 bond, and the other two (m/e 257 and 239) by consecutive elimination of two H₂O molecules. The expected



metastable transitions attributable to the two elimination processes (*a*) \rightarrow (*b*) *ca.*, m/e 240 and (*b*) \rightarrow (*c*), *ca.*, m/e 222.2 were present. In addition a third low intensity "metastable peak" was detected at *ca.*, m/e 207.8-208 in each case. The "metastable peaks" at *ca.* m/e 208 formally could correspond to the process (*a*) \rightarrow (*c*) (Calc., 207.7).

Evidently the C-5 double bond is not necessary for the process. The saturated 19(*R*)-acetoxy-derivative (IIc) gave the m/e 277 ion and had peaks corresponding to the sequential loss of two molecules of water at m/e 259 and 241. The latter elimination processes were accompanied by two "metastable ions", m/e 242 and 224.5, corresponding to (*a'*) \rightarrow (*b'*) (M^* Calc., 242.2) and (*b'*) \rightarrow (*c'*) (M^* Calc. 224.3) transitions. In addition to a third "metastable ion" formally resulting from the simultaneous loss of two molecules of water in the field-free region of the mass spectrometer was found at *ca.*, m/e 210 [calc., for (*a'*) \rightarrow (*c'*) 209.7].

In contrast to the 19-acetoxy-derivatives (IIa) and (III), the triol (IIb) did not exhibit this behaviour. The cleavage of 9-10 bond in (IIb) was accompanied by the hydrogen migration,⁶

[†] The mass spectra were recorded on an Atlas CH-4 and Hitachi-Perkin Elmer RMU 6-D mass spectrometers. We thank Professor K. Biemann for the permission to use the Hitachi mass spectrometer.

and the resulting m/e 276 ion (d) did not lose two H_2O molecules.

Recently, improved methods of detecting⁷ and assigning the origin⁸ of "metastable transitions" have been evolved. The present results demonstrate that in certain instances the detection of a "metastable" transition may not necessarily indicate that it was caused by a true single-step loss of a neutral particle.

[*Added in proof.*—Recently several similar cases have come to our attention.⁹ In one instance^{9c} the "metastable peak" was considered indicative of a true one-step loss of two molecules of carbon monoxide and on this basis a skeletal rearrangement of the molecular ion was suggested.]

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¹ N. J. Turro, D. C. Neckers, P. A. Leermakers, D. Seldner, and P. D'Angelo, *J. Amer. Chem. Soc.*, 1965, **87**, 4097.

² N. Maoz, A. Mandelbaum, and M. Cais, *Tetrahedron Letters*, 1965, 2087.

³ D. C. DeJongh, S. C. Perrione, and W. Korytnyk, *J. Amer. Chem. Soc.*, 1966, **88**, 1233.

⁴ K. R. Jennings, *Chem. Comm.*, 1966, 283.

⁵ E. Caspi and J. Wicha, *Chem. Comm.*, 1966, 209, 316. The (S)-alcohol was prepared by a different route and its synthesis will be reported elsewhere.

⁶ Cf., S. H. Eggers, *Tetrahedron Letters*, 1965, 733.

⁷ K. R. Jennings, 15th Annual Symposium on Mass Spectrometry, Denver, Colorado, May 1967.

⁸ R. E. Rhodes, M. Barber, and R. L. Anderson, *Analyt. Chem.*, 1966, **38**, 48; N. R. Mancuso, S. Tsunakawa, and K. Biemann, *ibid.*, 1966, **38**, 1779; A. Mandelbaum, *Israel J. Chem.*, 1966, **4**, 161.

⁹ (a) J. Seibl, *Helv. Chim. Acta*, 1967, **50**, 236; (b) H. Budzikiewicz, F. von der Haar, and H. H. Inhoffen, *Annalen*, 1967, **701**, 23; (c) R. M. Letcher and S. H. Eggers, *Tetrahedron Letters*, 1967, 3541.