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MASS SPECTROMETRY AND ORGANIC ANALYSIS. XI[1)]
THE MASS SPECTRUM OF β-IONONE

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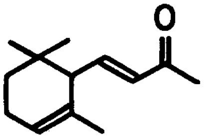
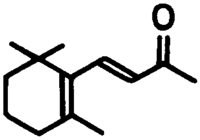
The mass spectra of the ionones are frequently quoted in standard textbooks[2,3)] to illustrate differences that can occur by virtue of different double bond positions. The molecular ion of α-ionone (I) undergoes a retro-Diels-Alder reaction, but that from β-ionone (II) loses a methyl group, usually assumed to be one of the allylic gem-dimethyls. The latter explanation seemed unlikely, since notwithstanding the generally less favourable loss of a methyl radical if other fissions are available[4,5)], the $(M-15)^+$ fragment constitutes 16.7% of the total ionization of β-ionone[2)], and this despite the fact that the carbonium ion generated would result in cross-conjugation with the π-system already present in the molecule.



I



II

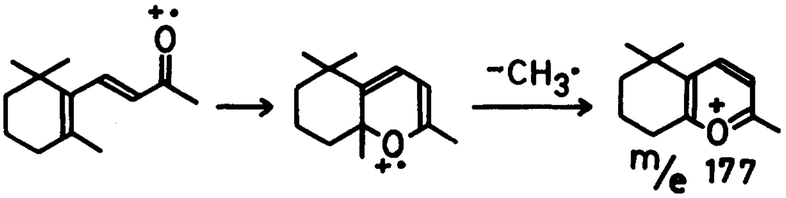
Mursakulov et al.[6)] have recently described the cyclization of pseudo-ionone in D_2SO_4, which they found led to a deuteriated β-ionone having none of the deuterium in the methyl group attached to the double bond, as measured from the n.m.r. spectrum, but with 3-5 hydrogens exchanged from the gem-dimethyl group and the adjacent ring methylene. On the other hand, van't Hof et al.[7], using a more concentrated solution, found 0.4 D in the vinyl methyl and 0.7 D in each gem-methyl. Using the Russians' conditions[*] we found for the two positions that interest us in the present context, about 0.2 D incorporated in the vinyl methyl and a total of 1.7 D into the gem-dimethyl group, with an isotopic distribution as shown in the table. Although a more specifically deuteriated β-ionone is required before quoting an exact figure, there is probably less than 25% of the methyl lost from the gem-dimethyl group.

TABLE

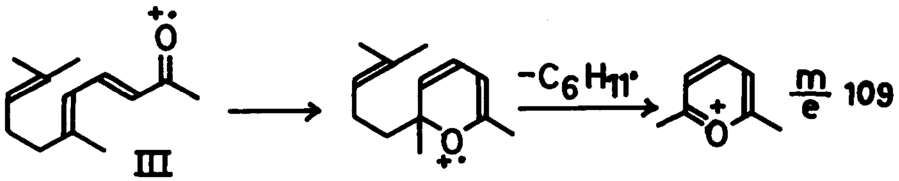
Isotopic Content of Molecular Ion and $(M-15)^+$.

	$\%d_1$	$\%d_2$	$\%d_3$	$\%d_4$	$\%d_5$	$\%d_6$
$M^{+\cdot}$	14	22	23	18	11	5
$(M-15)^+$	15	23	23.5	17.5	10	4.5

A reasonable explanation for the stability of the $(M-15)^+$ ion follows the photochemical reactions of β-ionone[8,9,10]:



It is interesting that there is a fragment at m/e 109 in the mass spectrum of pseudo-ionone (III), corresponding to loss of C_6H_{11} (see figure), which is most easily explicable by a cyclization of a similar type, followed by loss of the larger substituent from the quaternary carbon:



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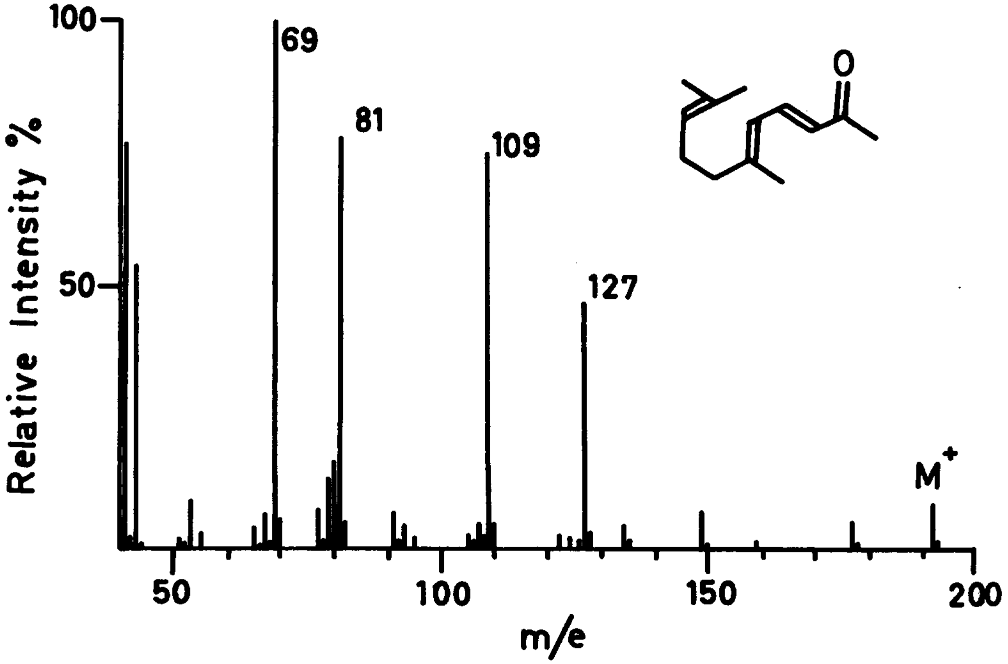
[*] Pseudo-ionone (0.5 g) in 3 ml nitropropane added at 10° to 0.75 ml (0.39 g) D_2SO_4 in 3 ml nitropropane.

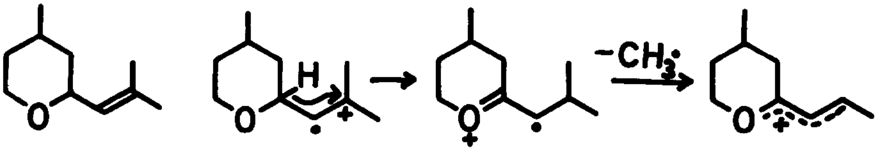
We should like to emphasize the need for having a stable ion to explain an exceptionally large loss of methyl radical, and draw attention to the possibility that rose oxide (IV) does not simply lose the 4-methyl group to give a $(M-15)^+$ fragment that constitutes 17.7% of the total ionization[2]. Perhaps a hydrogen rearrangement first takes place[11], leading,

FIGURE

The Mass Spectrum of Pseudo-ionone (cis-trans Mixture)



by loss of a methyl group originally attached to the double bond, to the stable ion (V).



IV V

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