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ELECTRON IMPACT INDUCED FRAGMENTATION OF CYCLIC KETONES FUSED TO A CYCLOBUTANE RING

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The use of mass spectroscopy for structural elucidation of organic compounds containing one or more cyclobutane rings is becoming increasingly widespread. The most important fragment corresponds to the cleavage, invariably giving a base peak, of the cyclobutane ring.[1] Based on this Ziffer and coworkers recently reported the use of chemical ionisation mass spectrometry to differentiate between the head-to-head (h-h) and the head-to-tail (h-t) photodimers of cyclic α,β-unsaturated ketones.[2] The h-t photodimer, in the presence of methane, gave a strong fragment corresponding to m/e [(M/2)+1], while the same fragment in the case of the h-h photodimer was very weak.

In connection with other studies, we had opportunity to examine the mass spectra of number of cyclic ketones fused to a cyclobutane ring.[3] The intriguing differences we observed in their spectra prompts us to report the result of our findings below.

The 70ev mass spectrum of the tricyclic ketone I (Fig. a)[4] showed a weak molecular ion peak at m/e 234 (1%) and low-intensity peaks corresponding to the ions resulting from cleavage of the cyclobutane ring at m/e 152 (10%) and m/e 82 (8%). In contrast, a strong peak at m/e 153, as the base peak, was observed. Examination of molecular models indicated proximity of the γ-hydrogens to the carbonyl group. We attribute, thus, the observed fragmentation pattern to the molecule undergoing preferential McLafferty rearrangement by transfer of one of the γ-hydrogens, to give Ib, over cleavage of the cyclobutane ring. The molecular ion, Ib, should readily cleave to give Ic, m/e 153, and the cyclo-

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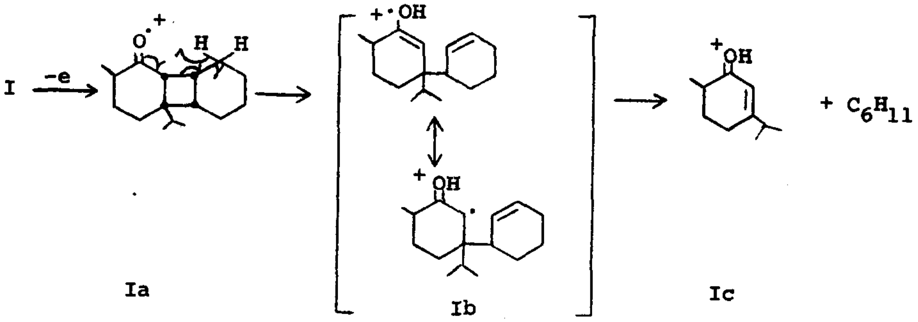
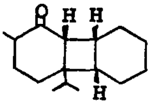
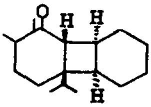
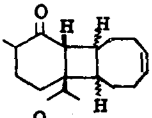
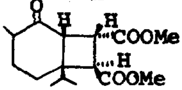
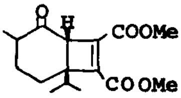
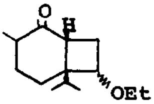


hexenyl radical. This argument is supported by the observation that the tricyclic ketones II and III, both of which contain proximate γ-hydrogens[5] also showed a strong peak at m/e 153 as the base peak (see Table 1), while the bicyclic ketones IV-VI, devoid of suitably positioned γ-protons, exhibited

TABLE 1

Relative Abundance of Important Mass Spectral Fragments of Cyclic Ketones I-VI.

No.	Compound	m/e=M	m/e=152	m/e=153
I		1 %	10 %	100 %
II		1.5	7.5	100
III		10	27	100
IV		10	94[a]	16
V		14	40[b]	11
VI		2	23[c]	2.7

a) m/e 110 (100%); b) m/e 41 (100%) and m/e 110 (50%); c) m/e 43 (100%) and m/e 110 (55%).

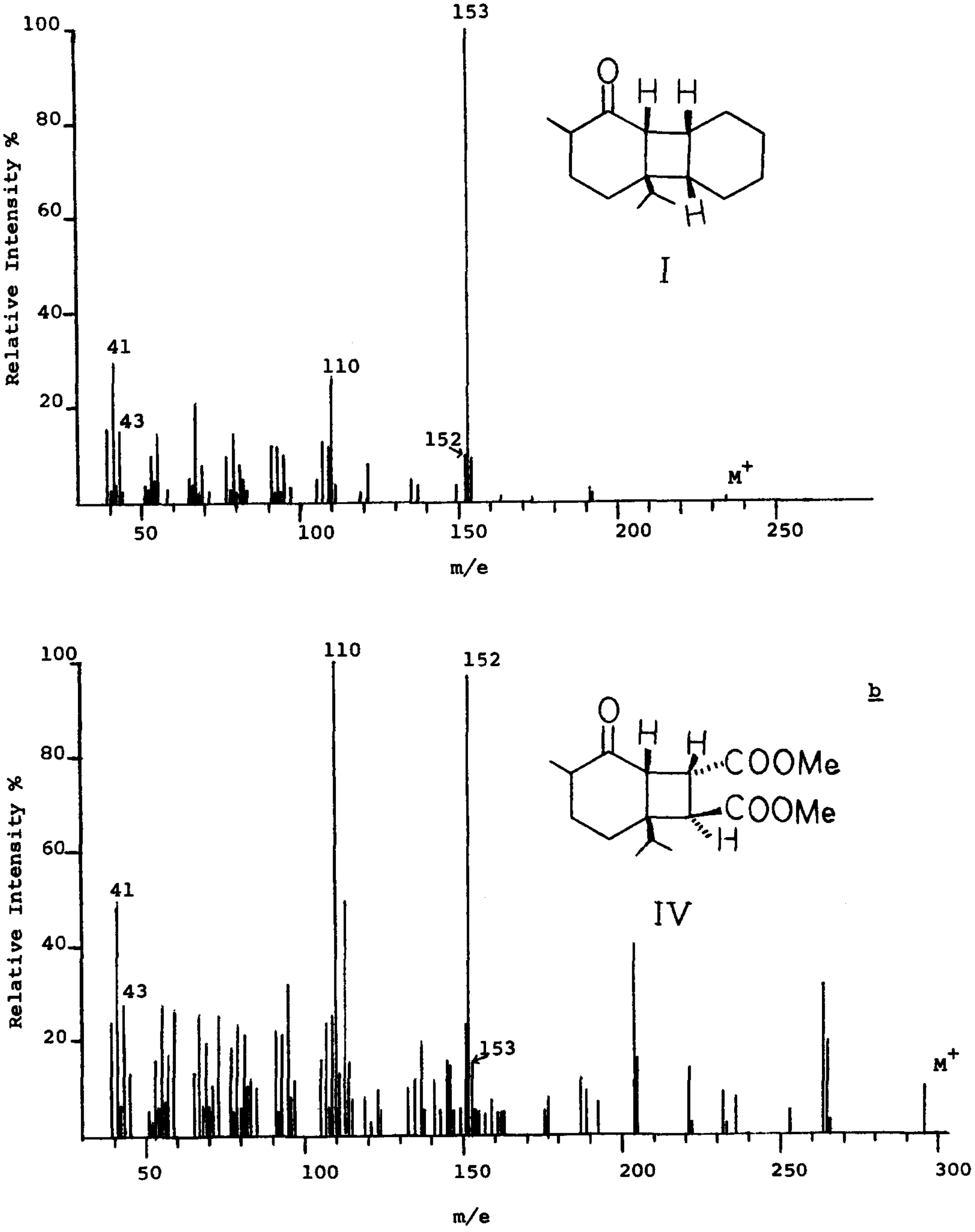
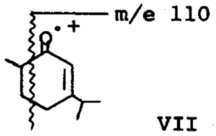


Fig. a Mass spectra of (a) tricyclic ketone I, (b) bicyclic ketone IV.

normal cyclobutane cleavage to give an abundant fragment, VII, at m/e 152. These compounds, however, showed an intense peak at m/e 110, attributed to



VII m/e 152

further fragmentation of the ion VII (metastable at m/e 79.6).[6] The bicyclic ketone VI gave, on electron impact, its base peak at m/e 43 due to the cleavage of the isopropyl group, while the ketone V gave its base peak at m/e 41 due to further loss of protons from the isopropyl ion.[7]

On the basis of the above results, it is conceivable that the fragments at m/e [(M/2)+1] observed in the chemical ionisation mass spectra of the (h-t) photodimers of cyclic α,β-unsaturated ketones[2] arise, at least in part, by intramolecular hydrogen transfer before cleavage of the cyclobutane ring.

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4. Mass spectra were recorded on an MS12 mass spectrometer.
5. The γ-hydrogens in the tricyclic ketone II are not as close to the carbonyl group as in the ketone I. However, a slight distortion of the molecule, II, conceivably undergoing rapidly at such a high energy as 70 ev, could suitably place these protons for an efficient intramolecular hydrogen transfer.
6. H. Budzikiewies, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco (1967), p. 153.
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