nmr δ CCl_4 3.50 (1 H, broad methine multiplet), 1.8–2.7 (8 H, complex multiplet for the ring methylene protons).

3-Trinitromethylcyclopentanone.—A solution of 2-cyclopentenone ethylene ketal (5.0 g, 0.04 mole) in 10 ml of 50% aqueous methanol was added to a solution of nitroform (6.0 g, 0.04 mole) in 50 ml of 50% aqueous methanol. The title compound was isolated and purified in the same manner as described for 3-trinitromethylcyclohexanone. The yield was 64%: mp 70°; nmr δ CCl_4, 3.9 (1 H, broad methine multiplet), 2.5 (6 H, multiplet for the ring protons).

Registry No.—2,2-Divinyl-1,3-dioxolane, 15353-18-1.

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Electron-Impact Fragmentations of $\Delta^{1(7)}$-Menthenone-2 and $\Delta^{8(9)}$-Menthenone-2

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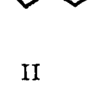
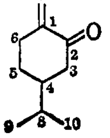
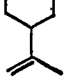
Details of the behavior of camphor (I) upon electron impact have been reported by Weinberg and Djerassi.[1] They have observed that (1) all of the major peaks in the mass spectrum of camphor are due to hydrocarbon species and the carbonyl group does not compete effectively with the hydrocarbon framework in directing the fragmentation of this molecule; (2) camphor and its isomer, *trans*-8-methylhydrindan-2-one (II), display very similar mass spectra, the principal difference residing only in the relative intensity of certain peaks; and (3) many of the fission reactions are best rationalized by postulating migrations of double bonds, alkyl groups, or hydrogen.


I


II



III


IV

In connection with our pyrolysis study,[2] mass spectra of two further isomers of camphor, $\Delta^{1(7)}$-menthenone-2 (III) and $\Delta^{8(9)}$-menthenone-2 (IV) were obtained, which are reproduced in Figures 1 and 2, respectively.[3] Although the mass spectral peak positions of these compounds are generally similar to those of camphor, detailed study using deuterium-labeling and high-resolution techniques shows that much difference exists among the electron-impact fragmentation reactions of these compounds.

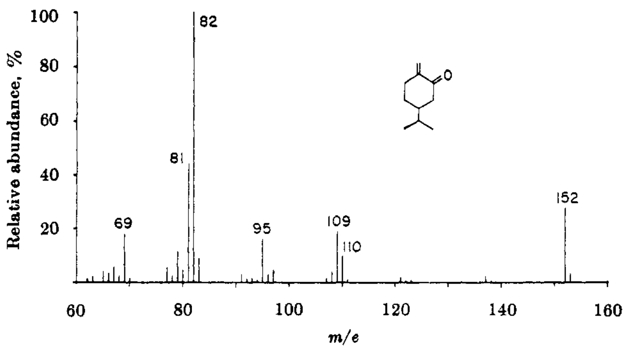


Figure 1.—Mass spectrum of $\Delta^{1(7)}$-methenone-2 (III).

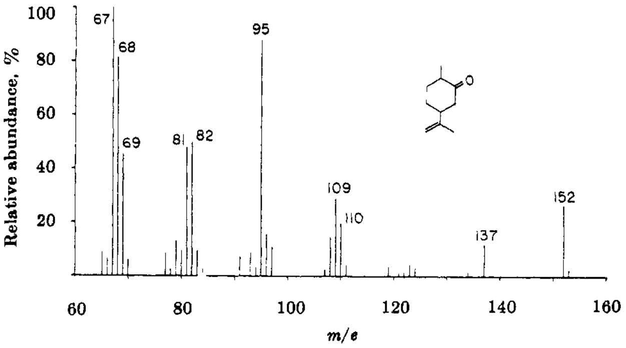


Figure 2.—Mass spectrum of $\Delta^{8(9)}$-methenone-2 (IV).

The principal mass spectral peaks (elemental compositions) of III determined by high-resolution measurement[4] are listed in Table I. High-resolution measurement was also carried out with III-3,3-d_2 and peaks were correlated to those of the nondeuterated analog. Unlike the case with camphor, most of the peaks are found to be doublets—a hydrocarbon ion peak and an oxygen-containing ion peak. It might be possible to write fragmentation mechanisms from these data, but there is not sufficient evidence to exclude alternatives explicitly and we avoid giving fragmentation mechanism in unwarranted detail.

TABLE I[a,b]

PRINCIPAL MASS SPECTRAL PEAKS OF III AND THEIR DEUTERIUM SHIFTS IN THE 3,3-d_2 ANALOG

Elemental compositions	
III	III-3,3-d_2
C_8H_{14} (110)	C_8H_{14} (110)
$C_7H_{10}O$ (110)	$C_7H_8D_2O$ (112)
C_8H_{13} (109)	$C_8H_{11}D_2$ (111)
C_7H_9O (109)	$C_7H_7D_2O$ (111)
C_7H_{11} (95)	C_7H_{11} (95)
C_6H_7O (95)	$C_6H_5D_2O$ (97)
C_5H_6O (82)	C_5H_6O (82), C_5H_5DO (83), $C_5H_4D_2O$ (84)
C_6H_9 (81)	$C_6H_7D_2$ (83)
C_5H_9 (69)	C_5H_9 (69)
C_4H_5O (69)	C_4H_5O (69)

[a] High-resolution mass spectra were recorded on a photographic plate and the peak intensities were not determined quantitatively. It is definitely shown, however, that the elemental compositions and their deuterium shifts shown in the table constitute the major portions of the spectra. [b] Figures in the parentheses designate *m/e*.

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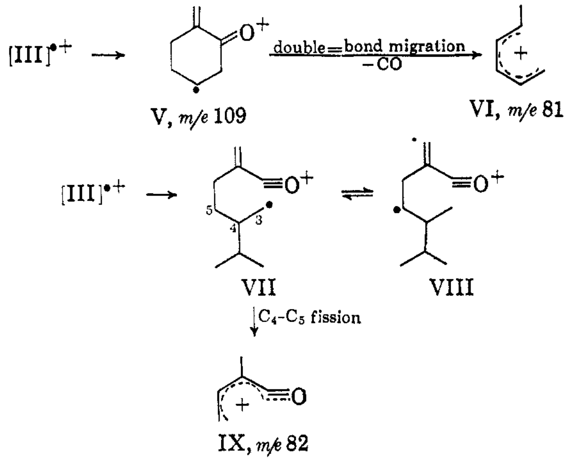
(1) D. S. Weinberg and C. Djerassi, *J. Org. Chem.*, **31**, 115 (1966).

(2) T. Sato, K. Murata, A. Nishimura, T. Tsuchiya, and N. Wasada, *Tetrahedron*, **23**, 1791 (1967).

(3) The mass spectra were determined on a CEC 21-103C mass spectrometer, the electron energy being 70 eV.

(4) The mass spectra were determined on a CEC 21-110B mass spectrometer, the electron energy being 70 eV.

Scheme I



The mechanism (V → VI, Scheme I) is substantiated by a metastable ion at m/e 60.3 ($81^2/109 = 60.2$). In support of this mechanism, the peak shifts to m/e 62.3 in the spectrum of III-3,3-d_2 ($83^2/111 = 62.2$).

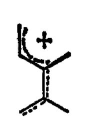
It is notable that $C_5H_6O^+$ (m/e 82) ion splits into a triplet upon deuteration. A rapid radical migration (VII $\rightleftharpoons$ VIII, Scheme I) is proposed by which an equilibrium between the hydrogen on C_3 and C_5 is attained prior to the C_4–C_5 bond fission in VII. This justifies the observation that ion IX gives rise to three peaks at m/e 82, 83, and 84 in the spectrum of d_2 species. Similar effects of equilibrium of hydrogen migration are observed in the spectrum of IV (*vide infra*).

Table II[a]

Principal Mass Spectral Peaks of IV and Their Deuterium Shifts in the 3,3-d_2 Analog

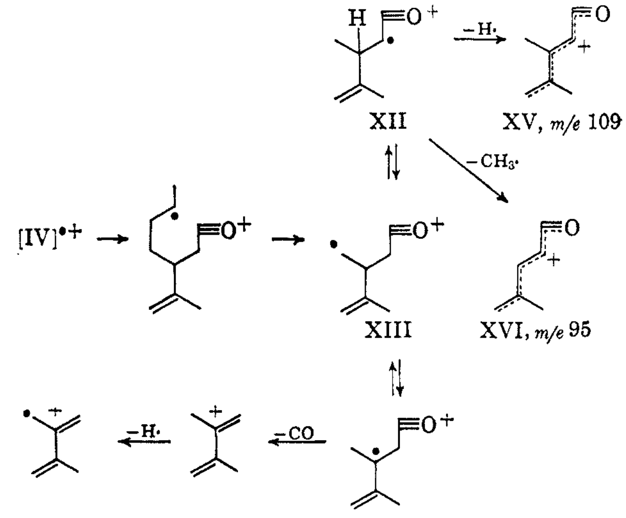
Elemental compositions	
IV	IV-3,3-d_2
$C_9H_{13}O$ (137)	$C_9H_{11}D_2O$ (139)
C_8H_{14} (110)	C_8H_{14} (110)
$C_7H_{10}O$ (110)	$C_7H_8D_2O$ (112)
C_8H_{13} (109)	C_8H_{13} (109), $C_8H_{11}D_2$ (111)
C_7H_9O (109)	C_7H_8DO (110), $C_7H_7D_2O$ (111)
C_8H_{12} (108)	C_8H_{12} (108)
C_7H_{11} (95)	C_7H_{11} (95), $C_7H_9D_2$ (97)
C_6H_7O (95)	C_6H_7O (95), C_6H_6DO (96), $C_6H_5D_2O$ (97)
C_6H_{10} (82)	$C_6H_8D_2$ (84)
C_5H_6O (82)	C_5H_6O (82)
C_6H_9 (81)	C_6H_9 (81), C_6H_8D (82), $C_6H_7D_2$ (83)
C_5H_9 (69)	$C_5H_7D_2$ (71)
C_4H_5O (69)	C_4H_5O (69)
C_5H_8 (68)	C_5H_8 (68), C_5H_7D (69), $C_5H_6D_2$ (70)
C_5H_7 (67)	C_5H_7 (67), C_5H_6D (68), $C_5H_5D_2$ (69)

[a] See footnotes in Table I.


X, m/e 95


XI, m/e 95

Scheme II



High-resolution measurements[4] were carried out on IV and IV-3,3-d_2. Each of the elemental compositions in the spectrum of IV is correlated to that of deuterated analog in Table II. It is noted that several peaks in the spectrum of IV split into doublets or triplets upon deuteration. Two postulations are set forward in order to rationalize the results. First, it is proposed that some ions are not due to single species. For example, both X and XI are proposed for the ion $C_7H_{11}^+$ (m/e 95). The former will shift to m/e 97 while the latter will remain at m/e 95 upon deuteration. Second, an equilibrium among C_3, C_4, and C_5 hydrogen (XII $\rightleftharpoons$ XIII $\rightleftharpoons$ XIV) prior to the loss of methyl or hydrogen from XII or carbon monoxide from XIV is proposed (Scheme II). This justifies the observations that (1) ion XV (m/e 109) gives rise to two peaks at m/e 110 and 111, (2) ion XVI (m/e 95) gives rise to three peaks at m/e 95, 96, and 97, and (3) ion XVII (m/e 81) gives rise to two peaks at m/e 82 and 83 in the spectrum of d_2 species. The splitting of the ions $C_5H_8^+$ (m/e 68) and $C_5H_7^+$ (m/e 67) upon deuteration is rationalized by the postulation of similar equilibrium of hydrogen migration.

In conclusion, it was found that these relatively simple monocyclic ketones undergo quite complicated fragmentation and the fragmentation would involve the double bond and radical migrations. It was also found that while all of the major peaks in the mass spectrum of camphor were due to hydrocarbon species, those of III and IV were due to hydrocarbon and oxygen-containing species. This implies that III and IV, which are the pyrolysis products of camphor, are not concerned to any extent in the electron-impact fragmentation of camphor.

Registry No.—III, 15297-07-1; III-3,3-d_2, 15297-08-2; IV, 5948-04-9; IV-3,3-d_2, 15297-10-6.

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