Electron Impact-induced Migrations in Cyclic Allylic Alcohols and Cyclic Enones

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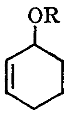
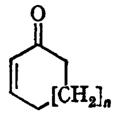
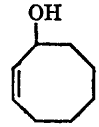
DURING the examination of the mass spectra of allyl-substituted cyclohexenes it was observed that the allylic alcohol (I) and its methyl ether (II) exhibited intense $M-15$ fragments (Table). For (I) this methyl group was shown by deuterium labelling to originate from C-6 together with one hydrogen from C-4 (the Scheme). This fragmentation mechanism is analogous to that reported[1] for the $M-15$ fragment in the spectrum of cyclohexene. This process is general for the enones [(III)–(VI)] which respectively exhibit $M-$methyl; $M-$ethyl; $M-$propyl, and $M-$butyl fragments. Analogous species occur in the spectra of the corresponding medium ring allylic alcohols, *e.g.*, (VII) and (VIII). The dominence of the process depicted in the Scheme is shown by a comparison of spectra of isophorol (IX) and β-isophorol (X).



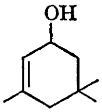
(I) R=H
(II) R=Me



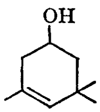
(III) $n=1$
(IV) $n=2$
(V) $n=3$
(VI) $n=4$



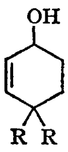
(VII) *cis*-
(VIII) *trans*-



(IX)



(X)



(XI) R=Me
(XII) R=Ph

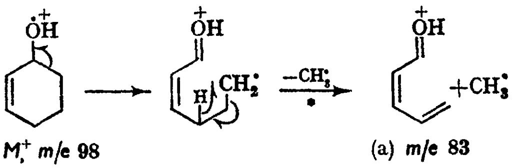
That of (IX) has the expected intense $M-15$

TABLE

Major fragments in the mass spectra of some cyclic allylic alcohols and cyclic enones

Compound	M^+		$M-H_2O$		*a*		Base peak	
	m/e	%	*m/e*	%	*m/e*	%	*m/e*	Composition†
(I)	98	49	80	8	83	30	70	C_4H_6O
(II)	112	97			97	48	84	C_5H_8O
(III) ..	96	38			81	2	68	C_4H_4O
(IV) ..	110	45			81	100	81	C_5H_7O
(V)	124	41			81	100	81	C_5H_7O
(VI) ..	138	24	120	8	81	100	81	C_5H_7O
(VII) ..	126	38	108	24	83	100	83	C_5H_9O
(VIII) ..	126	16	108	11	83	100	83	C_5H_9O
(IX) ..	140	27	122	10	125	100	125	$C_8H_{13}O$
(X)	140	20	122	18	(125	31)‡	107	C_8H_{11}
(XI) ..	126	8	108	3	97	6	70	$C_4H_6O(85\%)$ $C_5H_{10}(15\%)$
(XII) ..	250	30	232	20	159	55	206	$C_{16}H_{14}$

† Determined by high resolution measurements.
‡ Intensity of $M-CH_3$ fragment for comparison with species (*a*) from (IX).



SCHEME

fragment,[2] whereas its isomer (X), even with the presence of a tertiary allylic methyl group, exhibits only a weak $M-15$ fragment.

Corresponding migration of alkyl and aryl groups from C-4 to C-6 in suitably substituted derivatives of (I) are shown by the spectra of (XI) and (XII) which exhibit $M-$ethyl and $M-$benzyl fragments respectively. The general nature of the process shown in the Scheme is currently being used to investigate the relative migratory aptitudes of substituents in 4,4-disubstituted cyclohexanols for comparison with the migration of the same substituents in carbonium-ion or free-radical rearrangements.[3]

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[1] H. Budzikiewicz, J. I. Brauman, and C. Djerassi, *Tetrahedron*, 1965, **21**, 1855.

[2] Contribution to the $M-15$ peak in (IX) by the vinyl methyl group due to a fragmentation similar to that established for piperitol by A. F. Thomas, B. Willhalm, and J. H. Bowie, *J. Chem. Soc.* (*B*), 1967, 392, cannot be excluded.

[3] See, *e.g.*, E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt, New York, 1959, pp. 607 and 758.