of this research and to the University of Manitoba for a graduate student Fellowship awarded to one of us (C. U. L.). We extend our thanks to Mr. C. Reichert and Dr. J. Westmore of this department for the mass spectra and interpretation thereof.

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Electron impact-induced rearrangements of acetylenic compounds[1]

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The mass spectra of all-*trans*-hepta-2,4-dien-6-yn-1-ol (3) and all-*trans*-hepta-2,4-dien-6-yn-1-al (6) are remarkably similar to benzyl alcohol and benzaldehyde respectively. Comparison of α-*d*-all-*trans*-hepta-2,4-dien-6-yn-1-ol (5) and α-*d*-benzyl alcohol shows that the deuterium in the $C_7H_7^+$ tropylium ion is randomized in both compounds.

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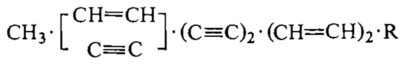
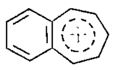
A problem of mass spectrometry concerns the formation of the $C_7H_7^+$ tropylium ion and other stable aromatic species. Acetylenic compounds of the type (**1**) undergo extensive rearrangement to give the $C_{11}H_9^+$ ion (**2**), as a major fragment (1). The C_7 acetylenic alcohol (**3**) possesses the yne-diene chromophore which is often contained in more complex polyacetylenes and upon electron impact affords a spectrum which resembles that of benzyl alcohol (**4**). A comparison of the fragmentation patterns is shown in Fig. 1. In addition it has been previously shown (3, 4) that the mass spectra of toluene and several of its acyclic C_7H_8 isomers are also similar, each giving a strong $C_7H_7^+$ tropylium ion. The formation of the $C_7H_7^+$ ion from benzyl alcohol (**4**) and several of its deuterated derivatives occurs with complete hydrogen (or deuterium) and carbon scrambling (5–8). Recently, however, Meyerson *et al.* (9) have shown that the statistics for diphenylmethane-α-d_2 fragmentation support tropylium-1,2-d_2 as the precursor for the $C_5H_5^+$ ion. Bohlmann and his co-workers (2) have examined the spectra of several acetylenic compounds in which both the $C_{11}H_9^+$ and $C_7H_7^+$ ions are assigned linear structures in which hydrogen scrambling has not occurred.



$CH_3\cdot\left[\begin{array}{c}CH{=}CH\\ C{\equiv}C\end{array}\right]\cdot(C{\equiv}C)_2\cdot(CH{=}CH)_2\cdot R$

1

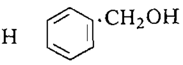


2

$R = -CH_2OH,\ -CH_2OAc,\ -CH_2CH_2CH_2OH,\ -(CH_2)_4\cdot CH{=}CH_2,\ -CH(OH)\,(CH_2)_3\cdot CH{=}CH_2$

$HC{\equiv}C\cdot CH{=}CH\cdot CH{=}CH\cdot CH_2OH$

3



4

We have now determined the mass spectrum of the deuterated alcohol (**5**) and compared it with that of α-*d*-benzyl alcohol. Examination of the $C_5H_5^+$ and $C_5H_4D^+$ ions indicates that for

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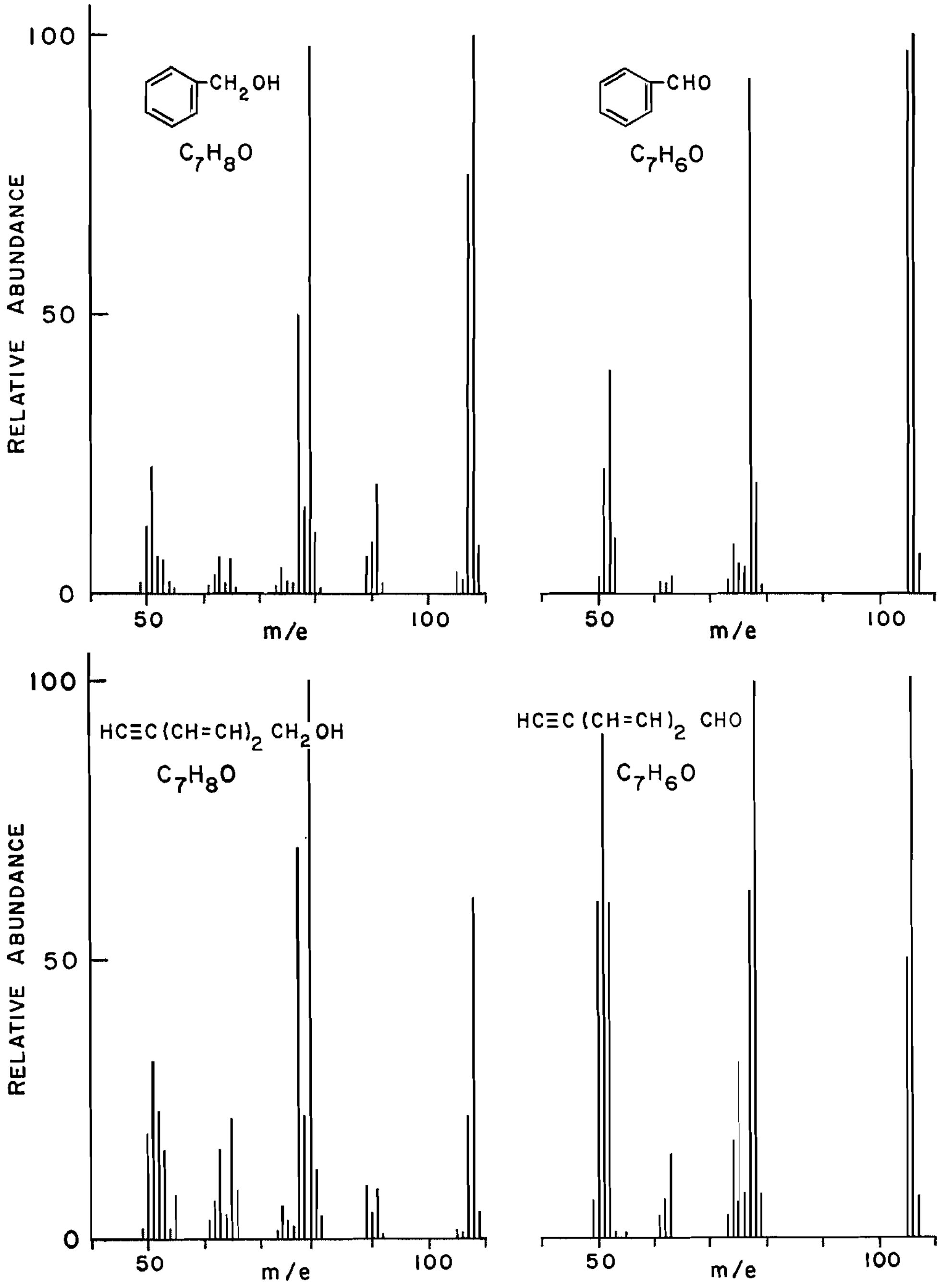


FIG. 1. A comparison of mass spectral fragmentation patterns.

the deuterated acetylenic alcohol (5), 74% of the deuterium is retained in the latter ion; the spectrum for α-*d*-benzyl alcohol shows 69% of the label retention (6) in the $C_5H_4D^+$ ion. These data are in agreement with 71% calculated for complete equilibration of the hydrogen atoms in the $C_7H_7^+$ precursor. The results obtained for the deuterated alcohol (5) and α-*d*-benzyl alcohol clearly indicate a common ion fragmentation pathway but the nature of the $C_7H_7^+$ ion, commonly designated as the tropylium moiety, is still not certain. The hydrogen atoms in the acetylenic alcohols (**6**) and (**7**) are also equilibrated (12) in their decomposition to $C_9H_7^+$ (*m*/*e* 115) represented as the indene ion (1).

$$HC{\equiv}C{\cdot}CH{=}CH{\cdot}CH{=}CH{\cdot}CHDOH$$

5

$$CH_3{\cdot}(C{\equiv}C)_3{\cdot}CH{=}CH{\cdot}CH_2OH$$

6

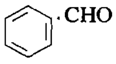
$$CH_3{\cdot}CH{=}CH{\cdot}(C{\equiv}C)_2{\cdot}CH{=}CH{\cdot}CH_2OH$$

7

A comparison of the mass spectra of the acyclic C_7 aldehyde (**8**) and benzaldehyde (**9**) is shown in Fig. 1. In both spectra metastable ions at m* 104 ($106 \xrightarrow{-\mathrm{H}\cdot} 105$), m* 76 ($78 \xrightarrow{-\mathrm{H}\cdot} 77$), and m* 56.4 ($105 \xrightarrow{-\mathrm{CO}} 77$) are observed. Since some evidence has been reported that acetylenic compounds give prominent linear ions (2) this result raises some doubt about the cyclic nature of the $C_6H_5^+$ ion (10) which is reported to be a prominent fragment in the mass spectra of benzaldehyde and several other monosubstituted phenyl derivatives.

$$HC{\equiv}C{\cdot}CH{=}CH{\cdot}CH{=}CH{\cdot}CHO$$

8



9

Experimental

Mass spectra were measured with a Consolidated Electrodynamics Corporation 21-110B instrument using electrical detection. Samples were introduced by effusion of vapor from a glass reservoir at 80 °. Several spectra in sequence showed constancy of the mass spectral patterns and absence of thermal reactions in the inlet system.

All-trans-hepta-2,4-dien-6-yn-1-ol (3)

The alcohol (**3**) was prepared by the method of Bohlmann *et al.* (11) in which Zincke aldehyde (all-*trans*-5-methylanilinopentadienal) is converted into all-*trans*-hepta-2,4-dien-6-yn-1-al (**6**) by the action of lithium acetylide in liquid ammonia; the alcohol is readily obtained by sodium borohydride reduction of the corresponding aldehyde.

All deuterated derivatives were prepared by sodium borodeuteride reduction of the corresponding aldehydes.

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Conformation of the esters of steroid hydroxyl groups by infrared spectroscopy

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Infrared spectral studies show that the carbonyl group of the esters of steroid hydroxyl groups are stabilized near the adjacent alkyl hydrogen atoms; this energy of stabilization appears to be more than that of hydrogen bonding between the carbonyl and a nearby hydroxyl group.

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In their extensive studies on the infrared (i.r.) spectra of steroids, Jones and co-workers (1) had found as early as 1951 from the spectra of a number of isomeric steroid C_3-acetates, that the equatorial C_3-acetate shows a single strong band in the region 1200–1260 cm^{-1}, whereas the axial one shows two or three strong bands in the same region. This empirical correlation has been of

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