data. Most important, however, is the establishment of the modest magnitude of ^{19}F SCS in the absence of a conjugated π electron system.[11d,29]

Experimental Section

^{19}F Chemical Shift Measurements. Reagent grade solvents were used without further purification. 1,1,2,2-Tetrachloro-3,3,4,4-tetrafluorocyclobutane (TCTFCB), obtained from Peninsular Chemresearch, Inc., Gainsville, Fla., was used without further purification. Hexafluorobenzene (HFB) was purified by distillation.

Measurements were made with Varian HR 56 and A56-60 instruments at 56.4 Mc on dilute solutions of the compound at probe temperature. Since most compounds are only slightly soluble in the solvents used, the chemical shift represents the intramolecular SCS at infinite dilution.

A side band on the internal reference was placed less than 200 cps from the desired signal. The frequency of the output signal was monitored electronically. The spectrum was swept in both upfield and downfield directions. The chemical shift, measured from the side band to the center of the signal plus the frequency of the side band, was taken as the average of the several upfield and downfield measurements.

The chemical shifts of the substituted compounds were referenced to the parent compounds in each series to define the SCS ($SCS_X = CS_X - CS_H$), where X represents the substituent, and CS_X and CS_H represent the chemical shift in ppm of the substituted and unsubstituted compounds relative to the internal reference (TCTFCB or HFB). In actual measurements TCTFCB and HFB were used as internal references for the 10-substituted 9-fluoroanthracenes and the bridged anthracenes, respectively. The maximum estimated error is 0.03 ppm and actual error is probably much less. It was demonstrated that the SCS agreed within less than 0.03 ppm when the parent compound was used as an additional internal reference.

Mass Spectrometry in Structural and Stereochemical Problems. CLXXIX.[1] The Electron Impact Induced Rearrangements of 1-Phenylheptenes. Further Evidence for Double Bond Lability[2]

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Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305. *Received June 2, 1969*

Abstract: The mass spectra of a series of isomeric 1-phenylheptenes have been measured. Evidence for extensive hydrogen and even phenyl rearrangement ions has been uncovered through the use of deuterium and ^{13}C-labeled analogs. Mass spectrometry is not a very useful tool for differentiating between such double bond isomers due to the ease of double bond migration after ionization.

During the course of our investigation into the electron impact induced rearrangements of organic compounds we observed that the mass spectra of a series of isomeric 1-phenylheptenes (I–V) exhibited many similar features (Figures 1–5).

This type of behavior seems typical of isomeric monoolefins in general, and there have been several reports attesting to similarities in the mass spectral fragmentation pattern of esters of unsaturated fatty acids,[4] isomeric menthenes,[5] phenylpropylenes,[6] and pentenes.[7] The phenomenon has been attributed to hydrogen rearrangements which result in a common mixture of molecular ions.[8] The mode of these rearrangement processes is not entirely clear and mechanisms involving 1,2-hydrogen,[9] 1,3-hydrogen,[10] and even more distant hydrogen shifts[11] have been invoked to explain the mass spectrometric behavior of simple olefins. In view of this diversity of mechanistic pathways, we have synthesized several isotopically labeled analogs of I and II (Table I) and examined their behavior upon electron

Table I. Comparison of Mass Shifts Encountered in the Isotopically Labeled Compounds for the *m/e* 117 Peak

Compd no.	Compound	% *m/e* 117 which shifts to[a] 117	118	119	120
VI	2,4,6-d_3-$C_6H_5CH{=}CHC_5H_{11}$			6	94
VII	$C_6H_5CH{=}CHCH_2CD_2C_3H_7$	95	5		
VIII	2,4,6-d_3-$C_6H_5CH_2CH{=}CHC_4H_9$			6	94
IX	$C_6H_5CD_2CH{=}CHC_4H_9$		12	88	
X	$C_6H_5CH_2CH{=}CHCD_2C_3H_7$	91	9		
XI	$C_6H_5CH_2CD{=}CDC_4H_9$		17	83	
XII	$C_6H_5{}^{13}CH_2CH{=}CHC_4H_9$	2	98		

[a] All the compounds have been corrected to 100% isotopic purity and the mass shifts calculated, after correcting for natural ^{13}C abundance, utilizing both the labeled and unlabeled mass spectra. Because of the errors in the mathematical procedure the results in the tables are considered to be only accurate to within 6% (J. Trudell Ph.D. Thesis, Stanford University, 1969).

(1) For paper CLXXVIII, see K. Strong, P. Brown, and C. Djerassi, Submitted for publication.

(2) We are indebted to the National Institutes of Health of the U. S. Public Health Service (Grants No. AM-04257 and AM-12758) for financial support.

(3) Postdoctoral Research Fellow, 1968–1969.

(4) B. Hallgren, R. Ryhage, and E. Stenhagen, *Acta Chem. Scand.*, 13, 845 (1959).

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

(6) Catalog of Mass Spectral Data, American Petroleum Institute, Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pa. Spectra No. 1210 and 1213.

(7) J. H. Benyon, R. A. Saunders, and A. E. Williams, "The Mass Spectra of Organic Molecules," Elsevier Publishing Co., Amsterdam, 1968, pp 63–65. See also W. Benz in "Methoden der Analyse in der Chemie, Band 8 Massenspektrometrie Organischer Verbindungen," Akademische Verlagsgesellschaft, Frankfurt am Main, 1969, p 397.

(8) For leading references, see H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1967, p 55.

(9) B. J. Millard and D. F. Shaw, *J. Chem. Soc.*, 13, 664 (1966).

(10) W. H. McFadden, *J. Phys. Chem.*, 67, 1074 (1963).

(11) F. W. McLafferty, *Anal. Chem.*, 31, 2072 (1959). See also G. Spiteller, "Massenspektrometrische Strukturanalyse Organischer Verbindungen," Verlag Chemie, Weinheim, 1966, pp 88, 97.

impact in an attempt to rationalize the processes giving rise to the observed mass spectra (Figures 1–5) of the isomeric 1-phenylheptenes. Compounds I–V were synthesized by standard procedures (see Experimental Section).

$C_6H_5CH{=}CHC_5H_{11}$
I

$C_6H_5CH_2CH{=}CHC_4H_9$
II

$C_6H_5CH_2CH_2CH{=}CHC_3H_7$
III

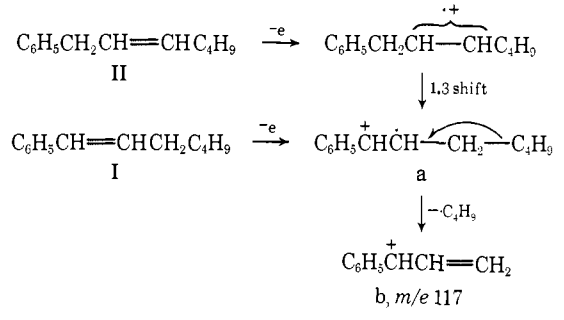
$C_6H_5CH_2CH_2CH_2CH{=}CHC_2H_5$
IV

$C_6H_5CH_2CH_2CH_2CH_2CH{=}CHCH_3$
V

Before proceeding to a discussion of the data, mention must be made of the possibility of thermal, metal-catalyzed isomerization prior to ionization. We consider that this can be discounted, since when pure samples of deuterated material were subjected to vapor phase chromatography at temperatures in excess of those used to determine their mass spectra, the samples were recovered unchanged. Their nuclear magnetic resonance (nmr) spectra showed that no deuterium scrambling occurred under these conditions. Moreover, the mass spectra of several compounds when determined on two separate instruments under widely differing conditions (see Experimental Section) gave almost identical mass spectra.

The M − C_4H_9 (*m/e* 117) Peak of the Phenylheptenes. The 70-eV spectra (Figures 1–5) of the isomeric heptenes all exhibit a substantial M − C_4H_9 fragment ion (*m/e* 117) which arises from the molecular ion, as evidenced by the presence of metastable peaks. The intensity of the *m/e* 117 peak declines to a minimum (Figure 3) and then increases in relative abundance as the double bond is moved progressively further away from the aromatic nucleus. At low voltage (12 eV) the peak becomes insignificant except for the spectrum of 1-phenylhept-5-ene (V) (*vide infra*), indicating that the process is one of high activation energy. In the case of the heptenes I and II, the deuterium-labeled compounds (Table I) indicate that approximately 90% of the fragment ion arises by a rearrangement in the molecular ion which involves a 1,3-hydrogen shift (Scheme I). The fact that no peak

Scheme I



occurs at M − C_5H_{11} in the mass spectrum of 1-phenylhept-1-ene (1) is in itself evidence of a rearrangement process.

The structure of the product ion b is only nominal and for the sake of brevity other resonance or ring-expanded representations are not depicted. It is of interest to

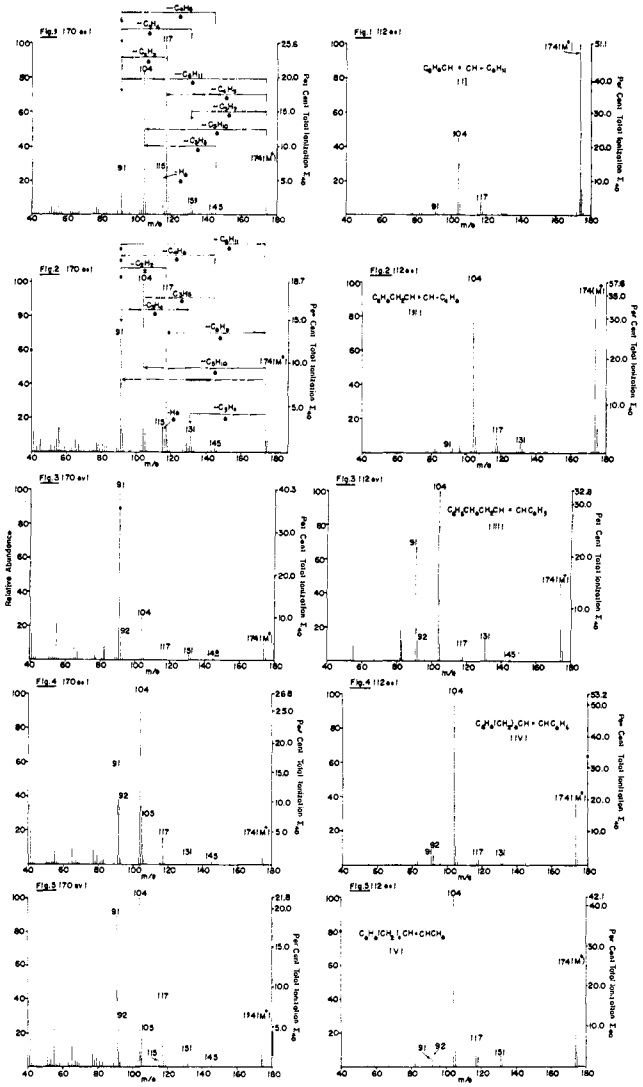


Figure 1. Mass spectrum of 1-phenylhept-1-ene at 70 and 12 eV.
Figure 2. Mass spectrum of 1-phenylhept-2-ene at 70 and 12 eV.
Figure 3. Mass spectrum of 1-phenylhept-3-ene at 70 and 12 eV.
Figure 4. Mass spectrum of 1-phenylhept-4-ene at 70 and 12 eV.
Figure 5. Mass spectrum of 1-phenylhept-5-ene at 70 and 12 eV.

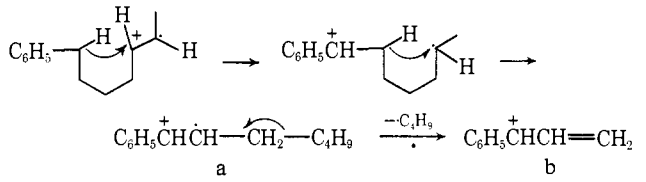
note that the mass spectra of 3-phenylprop-1-ene and cyclopropylbenzene[12] show a base peak at *m/e* 117 formed by loss of hydrogen from the molecular ion which lends support to the structure of ion b. If the same final step (a → b) of Scheme I intervenes in the fragmentation pathway of the isomeric heptenes III–V, then the final bond fission must be preceded by migration of the double bond to give ionized 1-phenylhept-1-ene (a).

We consider that such a process is indeed operating and that it is brought about by hydrogen rearrangement in the molecular ions. Support for this hypothesis is also noted from the data in Table I which indicates that a small amount (up to 17%, see XI in Table I) of deuterium scrambling occurs within the side chain. Also the relative intensity of the *m/e* 117 peaks in the mass spectra of the heptenes III, IV, and V is noticeably reduced (Figures 3, 4, and 5), presumably reflecting the greater difficulty encountered in the more distant migration of charge following initial ionization. The mode of these

(12) Reference 6, Spectrum No. 1963.

migrations is open to speculation and the present evidence suggests that they are not brought about by hydrogen rearrangements of any specific type. The presence of a peak at *m/e* 117 in the mass spectrum of V of appreciable relative intensity at both 70 and 12 eV (Figure 5) is readily explained (Scheme II) on the basis

Scheme II



of hydrogen transfer proceeding *via* a more energetically favorable six-membered transition state.[11]

The M − C_5H_{10} Rearrangement Peak (*m/e* 104). The most startling feature encountered in the mass spectra of the 1-phenylheptenes is the occurrence of an M − C_5H_{10} fragment ion which is observed at both high and low voltage. In the majority of cases it is the most significant peak at 12 eV. Examination of the origin of mass 104 ion in the spectra of compounds I and II using Jennings' metastable defocusing device[13] indicates that the fragment ion arises predominantly from the two ions of mass 174 and 145. However, examinations of the distribution of deuterium in the fragment ion encountered in the spectra of the deuterated analogs VI–X (Table II) indicates that the origin of the peak at *m/e* 104 is far from straightforward and several rearrangement pathways (Scheme III) must be postulated in order

Table II. Comparison of Mass Shifts and Peaks Resulting from the Proposed Processes for the *m/e* 104 Peak

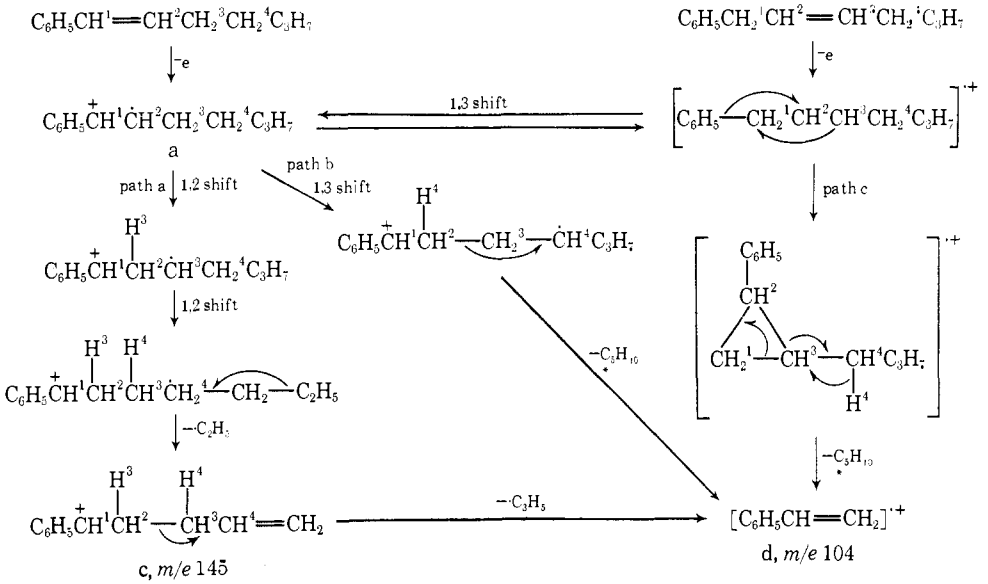
Compd no.	Peak formed by process C	D	E	% *m/e* 104 which shifts to: At 70 eV 104	105	106	107	At 12 eV 104	105	106	107
VI	107	107	107			12[a]	88			18[a]	82
VII	104	105	104	74	26			70	30		
VIII	107	107	107			12[a]	88			17[a]	83
IX	105, 106	105	106	4	45	51		23	51	26	
X	104	105	104	76	24			72	24	4	
XI	105, 106	105	105		82	18		4	80	16	
XII	105	105	105	2	98			2	98		

[a] The significance of these figures is discussed later under the heading "exchange between the aromatic nucleus and the side chain."

The mechanistic Scheme III, path b, involves a 1,3-hydrogen shift and logically follows from Scheme I as an alternative fragmentation pathway from ion a. The intervention of the process depicted in Scheme III, path c, is perhaps the most interesting since it requires the transfer of a phenyl group between adjacent carbon atoms. Mass spectral rearrangements involving the migration of a phenyl nucleus have been documented occasionally in the literature.[15] Moreover, the data (Table III) obtained from the ^{13}C-labeled 1-phenylhept-2-ene (XII) indicate that such migrations are also possible in the present series of compounds.

At low voltage (a nominal 12 eV) the mass shifts encountered for the *m/e* 104 peak indicate that a small

Scheme III



to account for the observed isotopic distribution.

Scheme III, path a, involves 1,2-hydrogen shifts which result in the formation of ion c (*m/e* 145) which then undergoes decomposition by elimination of a propylene radical to give ion d (*m/e* 104). Such hydrogen shifts are well documented in the literature, and Millard and Shaw[9] have elegantly demonstrated their participation in the breakdown of ionized pentenes. The structure of fragment ion d ("ionized styrene") is again purely nominal.[14]

amount of deuterium randomization may be occurring (Table II). A similar behavior has been noted in the low-voltage spectra of deuterated ethyl pentyl ketones[16] and Williams, *et al.*,[17] have offered an interesting ex-

(13) K. R. Jennings, *J. Chem. Phys.*, **43**, 4176 (1965).

(14) Ring expansion to ionized cyclooctatetraene has been suggested by E. I. Quinn and F. L. Mohler, *J. Res. Nat. Bur. Stand.*, **62**, 39 (1959).

(15) (a) P. Brown and C. Djerassi, *Angew. Chem. Intern. Ed. Engl.*, **6**, 477 (1967); (b) R. L. N. Harris, F. Komitsky, Jr., and C. Djerassi, *J. Am. Chem. Soc.*, **89**, 4765 (1967).

(16) W. Carpenter, A. M. Duffield, and C. Djerassi, *ibid.*, **90**, 160 (1968).

(17) A. N. H. Yeo, R. G. Cooks, and D. H. Williams, *Chem. Commun.*, 1269 (1968).

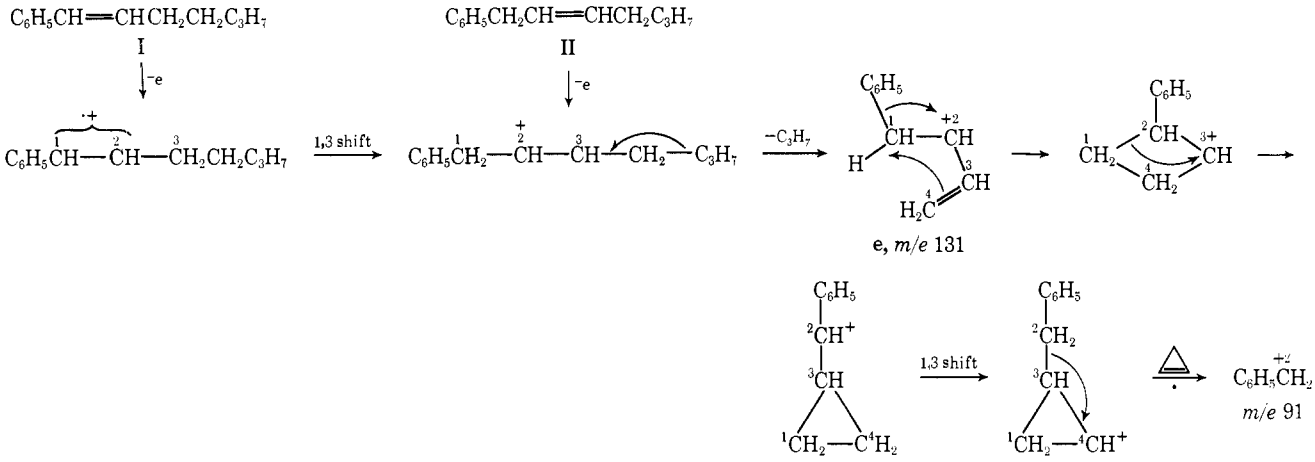
Table III. Comparison of Mass Shifts and Peaks Resulting from the Proposed Processes for the *m/e* 91 Peak

Compd no.	Peak formed by process F	G	H	% of *m/e* 91 which shifts to 91	92	93	94
VI	94	94	94			30[a]	70
VII	91, 92	91	91	74	26		
VIII	94	94	94			26[a]	74
IX	91, 92	92, 93	93	11	32	57	
X	91, 92	91	91	76	24		
XI	92	91, 92	91	63	37		
XII	91	92	92	21	79		

[a] An explanation of these figures is afforded in the section dealing with hydrogen exchange with the aromatic portion of the molecule.

planation of this phenomenon based upon ion lifetimes. If in the present case the parent ions possess relatively long lifetimes, then the partial deuterium randomization at low voltage is readily understood.

Scheme IV



The ion mass 104 in the spectra of the double bond isomers (III–V) presumably arises by similar mechanisms. The possibility of hydrogen transfer through six- or seven-membered transition states cannot be discounted and may contribute to the facility of the M − C_5H_{10} process at low voltage.

Formation of the Tropylium Ion. At high voltage the mass spectra of the 1-phenylheptenes all exhibit a fragment ion of mass 91 which most likely corresponds to the tropylium ion ($C_7H_7^+$).[18] The relative abundance of this ion becomes insignificant at 12 eV except for 1-phenylhept-3-ene (*vide infra*). An analysis of the metastable peaks[13] in the spectra of I and II showed that the *m/e* 91 peak arises from the precursor ions of mass 117, 131, 145, and 174. This diversity of mechanistic pathways is clearly reflected in the mass distribution in the tropylium ion (Table III) obtained from the deuterated analogs VI–XI.

Since the analog XII labeled with ^{13}C in the benzylic position still shows an appreciable amount of *m/e* 91 in addition to the expected *m/e* 92 peak, at least one of the mechanistic paths must involve migration of the phenyl group which is depicted schematically in Scheme IV.

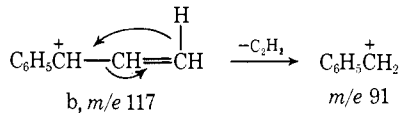
(18) H. M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, pp 516–519.

The loss of a propyl radical to give ion e is not unexpected. In accord with this sequence, the peak at *m/e* 91 in the mass spectrum (Figure 2) of II shifts to *m/e* 92 to a limited extent (79%) in the ^{13}C-labeled derivative (XII). Moreover, the proportion (11%) of the peak which remains at *m/e* 91 in the mass spectrum of the deuterated heptene (IX) is precisely the quantity which is predicted by this mechanism. It is of interest to note that Wagner[19] has suggested a substituted cyclopropane ion to explain the isomerizations which occur when pentenes and hexenes are radiated at elevated temperatures while Meisels, *et al.*,[20] have recently provided convincing evidence of the participation of skeletal rearrangement processes to give methylcyclopropene cation in the electron-induced fragmentation of but-1-ene.

The further decomposition of the ion of mass 117 also contributes significantly to the processes leading to the tropylium ion and presumably proceeds by elimination of acetylene from ion b (Scheme V).

A similar fragmentation is observed[6] in the mass spectra of 2-phenylprop-1-ene and 1-phenylpropan-

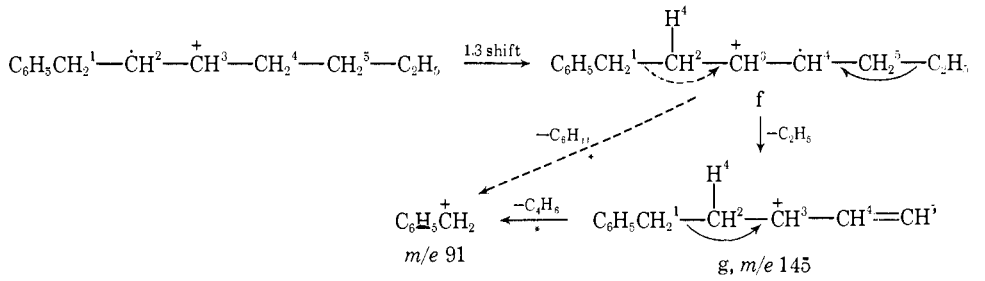
Scheme V



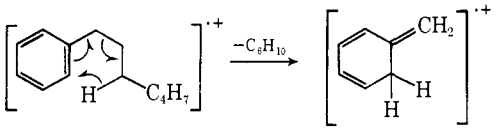
3-ol[21] which lends support to this proposed sequence. The mechanistic pathways which originate from the ions of mass 174 (M^+) and 145 are considered in Scheme VI. The base peak in the mass spectrum (Figure 3) of 1-phenylhept-3-ene (III) is at *m/e* 91. This is the only isomer which also has an abundant *m/e* 91 peak in its 12-eV spectrum. Both observations reflect the energetically favored bond fissions depicted in Scheme VI for ions f and g. Undoubtedly, similar pathways account for the fragment of mass 91 in the spectra of the other double bond isomers although, as evidenced by the mass spectrum of III in which the relative abundance of the tropylium ion is greatly enhanced, the relative contribution of the various mechanisms will undoubtedly be different.

(19) C. D. Wagner, *J. Phys. Chem.*, **71**, 3445 (1967).
(20) G. G. Meisels, J. Y. Park, and B. G. Giessner, *J. Am. Chem. Soc.*, **91**, 1555 (1969).
(21) N. M. M. Nibbering and Th. J. de Boer, *Tetrahedron*, **24**, 1415 (1968).

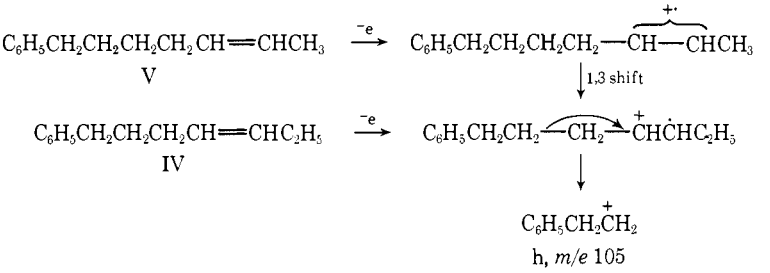
Scheme VI



Scheme VII

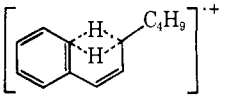


Scheme VIII



Isotope studies[17] have indicated that this occurs by fission of the benzylic bond with transfer of the hydrogen from the γ position. Consequently the greater relative abundance of the *m/e* 92 species in the mass spectra (Figures 4 and 5) of IV and V is readily understood since there will be no necessity for bond rearrangement prior to breakdown (Scheme VII). Indeed, the fact that this fragmentation scheme intervenes at all in the electron impact induced fragmentation of compounds I, II, and III is evidence in support of hydrogen migrations within the molecular ions. Compounds IV and V also show abundant $C_8H_9^+$ ions (*m/e* 105) in their mass spectra (Figures 4 and 5). This fragment ion is perhaps not unexpected in these compounds in view of the minimum charge rearrangement necessary prior to bond fission (Scheme VIII). More stable rearrangement forms (benzyl or tropylium ions) of ion h can undoubtedly be postulated.

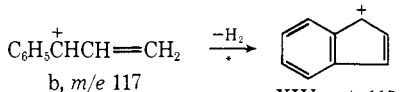
Exchange between the Aromatic Nucleus and the Side Chain. Examination of the data (Tables II and III) obtained for the deuterated compounds VI and VIII indicates that appreciable (up to 30%) exchange is occurring between the *ortho* hydrogens of the phenyl nucleus and the side chain. Nibbering and de Boer[21] have noted a similar phenomenon in the mass spectrum of γ-phenylpropanol. By utilizing deuterium-labeled compounds they showed that elimination of water occurred "before and after mutual exchange between the hydroxyl, γ and *ortho* hydrogen atoms in the molecular ion." Duffield, *et al.*,[22] have demonstrated that exchange also occurs between the ring and γ hydrogens during the electron impact induced breakdown of N-alkylpyrroles. In view of these observations, the present behavior is perhaps not unexpected and the present results can be accommodated by the intervention of an intermediate of type XIII (*cf.* ref 21).



XIII

Other Fragmentation Sequences. The mass spectra of the heptenes also exhibit several other peaks which are amenable to interpretation. A fragment ion of mass 92 is noticeable in the spectra of all the alkenes. The relative intensity of this peak in the spectra (Figures 1, 2, and 3) of compounds I, II, III, when corrected for the ^{13}C-isotope contribution from the adjacent peak (7.7% of the *m/e* 91 peak), becomes small. *n*-Alkylbenzenes of three or more aliphatic carbon atoms are known[17,23] to give an ion of mass 92 upon electron impact.

Finally, the fragmentation sequence *m/e* 117 → 115 is noted in all cases, m* 113.2 (calcd 113.1). This transition is also seen in the mass spectra of 1-phenylprop-2-ene,[6] cyclopropylbenzene, and γ-phenylpropanol.[21] An attractive formulation for the fragment ion of mass 115 is given by the various canonical forms of structure XIV.



b, *m/e* 117 XIV, *m/e* 115

General Conclusions

All the 1-phenylheptenes examined exhibit double bond mobility upon electron impact. The results obtained using the ^{13}C-labeled derivatives show that they have a marked propensity to undergo skeletal as well as hydrogen rearrangements. The presence of the phenyl nucleus undoubtedly influences the fragmentation pathway to a large extent. In view of the present behavior and the earlier literature citations,[5-7] it would seem that

(22) A. M. Duffield, R. Beugelmans, H. Budzikiewicz, D. A. Lightner, D. H. Williams, and C. Djerassi, *J. Am. Chem. Soc.*, 87, 805 (1965).

(23) R. B. Fairweather, F. W. McLafferty, and H. D. R. Schuddemage, *Org. Mass. Spectrosc.*, in press.

mass spectrometry is not a useful tool for differentiating among isomeric monoolefins.

Experimental Section

All mass spectra were determined by Mr. R. G. Ross on an AEI MS-9 mass spectrometer. The samples were introduced *via* the heated inlet system. All low voltage spectra correspond to nominal electron volt values. Some of the spectra were repeated on the Atlas CH-4 mass spectrometer by direct insertion of the sample into the E4-B ion source. In every case the spectra were the same as those determined on the AEI MS-9 instrument.

1-Phenylhept-1-ene (1). To a suspension on *n*-hexyltriphenylphosphonium bromide (4.27 g) in dry tetrahydrofuran (25 ml) was added a solution of *n*-butyllithium (6.2 ml, 1.6 *M* in hexane) followed by benzaldehyde (0.94 g) and the mixture stirred for 1 hr. The reaction mixture was poured into water (70 ml) and extracted with three 20-ml portions of pentane. The combined organic extracts were dried ($MgSO_4$) and the solvent was removed *in vacuo* to give a yellow oil which was distilled to yield the product (1.2 g), bp 76–79° (0.8 mm) (lit.[24] bp 120–122 (13 mm)). Final purification was afforded by preparative gas chromatography[26,26] at 160°.

Anal. Calcd for $C_{13}H_{18}$: mol wt, 174. Found: mol wt, 174 (mass spectrum).

1-Phenylhept-2-yne.[27] A solution of hex-1-yne (6 ml) in tetrahydrofuran (25 ml) was cooled (ice bath) and stirred under an atmosphere of nitrogen. *n*-Butyllithium (22 ml, 2.51 *M* in hexane) was added dropwise and the solution stirred 15 min and then allowed to warm to room temperature. Benzyl bromide (8.55 g) was added dropwise and the mixture heated under reflux during 4 hr. Water (40 ml) was added and the organic phase removed by extraction with two 20-ml portions of pentane. The combined extracts were dried ($MgSO_4$) and the solvent was removed. Distillation of the resulting yellow oil gave 1-phenylhept-2-yne (6.0 g), bp 60–63° (0.1 mm).

Anal. Calcd for $C_{13}H_{16}$: mol wt, 172. Found: mol wt, 172 (mass spectrum).

1-Phenylhept-2-ene (II).[27] To a cooled (ice bath) solution of disiamylborane in diglyme (2 ml) [prepared from 2-methylbut-2-ene (0.84 g), sodium borohydride (0.17 g), and BF_3 ethereate (0.8 ml) according to the procedure of Brown and Zweifel[28]] was added quickly the above acetylene. The resulting mixture was stirred for 0.5 hr at 0°, followed by 2 hr at room temperature. Ethylene glycol (2 drops) was added and the mixture cooled to 0°. Glacial acetic acid (2.5 ml) was added and the reaction maintained at room temperature for 2 hr and then poured into water (50 ml). The separated organic material was extracted into three 20-ml portions of pentane and the combined extracts were washed with three 20-ml portions of 10% sodium hydroxide solution and two 20-ml portions of water and finally dried ($MgSO_4$). Removal of the solvent followed by distillation of the resulting oil gave II (0.53 g), bp 53–55° (0.2 mm). Gas chromatography at 205° yielded a pure sample.[29]

Anal. Calcd for $C_{13}H_{18}$: mol wt, 174. Found: mol wt, 174 (mass spectrum).

1-Phenylhept-3-ene (III). To hydrocinnamyltriphenylphosphonium bromide (prepared by heating hydrocinnamyl bromide with triphenylphosphine under reflux in benzene for several hours and filtering the precipitated salt) (2.8 g) suspended in tetrahydrofuran (20 ml) was added *n*-butyllithium (3.5 ml, 1.6 *M* in hexane) followed by butyraldehyde (0.6 ml). After stirring for 1 hr the product was isolated in the same manner as I. Distillation of the reaction mixture gave III (0.83 g), bp 93° (2.5 mm), which was further purified by gas chromatography at 178°.

Anal. Calcd for $C_{13}H_{18}$: mol wt, 174. Found: mol wt, 174 (mass spectrum).

1-Phenylhept-4-ene (IV). The Grignard reagent of hydrocinnamyl bromide (40 g) and magnesium (5.4 g-atoms) was prepared in dry ether and poured onto crushed carbon dioxide. The acid was isolated and reduced to the corresponding alcohol with lithium aluminum hydride (8.0 g) in ether (180 ml) in the usual manner.[22] The crude alcohol was treated with hydrobromic acid (70 ml, 48%)–sulfuric acid (15 ml) at reflux temperature for 1.5 hr. Distillation to dryness followed by isolation of the bromide from the distillate by extraction into ether yielded a crude product which was purified by distillation to give 4-phenylbutyl bromide (8.2 g), bp 86–88° (0.7 mm). This bromide (4.0 g) was allowed to react with triphenylphosphine (5.4 g) in refluxing benzene (3 ml) to yield the phosphonium salt (4.9 g). Treatment of this salt with *n*-butyllithium followed by propionaldehyde as before yielded the desired product (0.9 g) which was isolated by distillation, bp 71–74° (0.8 mm). Final purification was achieved by gas chromatography at 175°.

Anal. Calcd for $C_{13}H_{18}$: mol wt, 174. Found: mol wt, 174 (mass spectrum).

1-Phenylhept-5-ene (V). Repetition of the above sequence of events using 4-phenylbutyl bromide gave 5-phenylpentyl bromide which was treated with triphenylphosphine to give the corresponding phosphonium salt (3.8 g). Treatment with butyllithium followed by acetaldehyde addition and work-up in the usual manner gave the desired olefin V (0.2 g) which was purified by gas chromatography.[30]

Anal. Calcd for $C_{13}H_{18}$: mol wt, 174. Found: mol wt, 174 (mass spectrum).

Benzyl Alcohol-2,4,6-d_3. Aniline-2,4,6-d_3 was prepared by exchange of the protons in aniline hydrochloride with D_2O according to a reported procedure.[31] Iodobenzene-2,4,6-d_3 was synthesized using this labeled material[32] which was subsequently converted to benzoic acid-2,4,6-d_3 by carbonation of the corresponding Grignard reagent with carbon dioxide. Reduction of this acid with lithium aluminum hydride followed by isolation of the product in the usual manner[22] gave benzyl-2,4,6-d_3 alcohol.

1-Phenylhept-1-ene-2′,4′,6′-d' (VI). Benzaldehyde-2,4,6-d_3 was prepared from the above benzyl alcohol by oxidation in refluxing benzene solution with activated manganese dioxide during 8 hr. The oxidizing agent was removed by filtration and the benzaldehyde obtained by evaporation of the solvent *in vacuo*. This was reacted further, without purification, to yield V; 96% V-d_3, 4% V-d_2.

1-Phenylhept-2-ene-2′,4′,6′-d_3 (VIII). Benzyl-2,4,6-d_3 bromide was prepared from the corresponding labeled benzyl alcohol by heating under reflux with a twofold excess of hydrobromic acid (48%) during 4 hr. Addition of water and extraction with ether gave the bromide in quantitative yield which was used without further purification to synthesize VIII; 96% VIII-d_3, 4% VIII-d_2.

1-Phenylhept-2-ene-1,1-d_2 (IX). This compound was synthesized from benzyl-α,α-d_2 bromide which was prepared by reduction of ethyl benzoate with lithium aluminum deuteride followed by treatment of the resulting deuterated benzyl alcohol with hydrobromic acid as described above.

1-Phenylhept-2-ene-2,3-d_2 (XI). This derivative was prepared from 1-phenylhept-2-yne by reduction with disiamylborane-B-d_1 (prepared from sodium borodeuteride, 2-methylbut-2-ene, and BF_3 etherate[28]) followed by protonolysis with acetic acid-d_4 to give XI; 82% XI-d_2, 18% XI-d_1.

1-Phenylhept-2-ene-4,4-d_2 (X). *n*-Propyl diethylmalonate was prepared by a standard procedure[33] and converted to pentyl-2,2-d_2 bromide by a reported sequence.[22] Formation of the phosphonium salt, treatment with butyllithium, and condensation with an equivalent amount of phenylacetaldehyde, in the same manner as described above, afforded the compound X; 96% X-d_2, 4% X-d_1.

1-Phenylhept-1-ene-4,4-d_2 (VII). Pentyl-2,2-d' bromide was homologated[22] to give hexyl-3,3-d_2 bromide which, when subjected to the same sequence of events used to synthesize I, yielded the required derivative VII; 96% VII-d_2, 4% VII-d_1.

1-Phenylhept-2-ene-1-^{13}C (XII). Treatment of bromobenzene (1.57 g) with magnesium (0.24 g) in ether (20 ml) afforded a solution of phenylmagnesium bromide which was carbonated at −40° with

(24) J. Normant, *Bull. Soc. Chim. Fr.*, 1888 (1963).

(25) The isomeric heptenes I–IV were purified by gas chromatography on a 10-ft, 15% Carbowax 20M on Chromosorb W column using an Aerograph A-90-P instrument, prior to the determination of their mass spectra.

(26) The two double bond isomers were separated from the distilled product by this method. Both exhibited identical mass spectra.

(27) We thank Dr. G. W. Adelstein for the synthesis of these compounds.

(28) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 3834 (1961).

(29) The two compounds I and II have widely differing retention times. On recycling a sample of II through the gas chromatogram no isomerization to give I was noted.

(30) A 10-ft column, 15% Ucon 50 LB 550 on Chromosorb G at 194°, was used to bring about the purification.

(31) A. P. Best and C. L. Wilson, *J. Chem. Soc.*, 239 (1946); see also R. I. Akawie, J. M. Scarborough, and J. G. Burr, *J. Org. Cem.*, **24**, 946 (1959).

(32) A. I. Vogel, "Practical Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1962, p 598.

(33) R. Adams and R. M. Kamm, "Organic Syntheses," Coll. Vol. I, John Wiley & Sons, Inc., New York, N. Y., 1932, p 250.

gaseous ^{13}C-enriched carbon dioxide (100 ml, 52% ^{13}C enriched). After destruction of the excess Grignard reagent with saturated ammonium chloride solution at −40°, work-up in the usual manner[22] gave the labeled benzoic acid (0.52 g). This was converted to benzyl-1-^{13}C bromide as outlined above which was then utilized to prepare XII.

Mass Spectrometry in Structural and Stereochemical Problems. CLXXXIII.[1] A Study of the Electron Impact Induced Fragmentation of Aliphatic Aldehydes[2]

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Abstract: In spite of the importance of the aldehyde functionality in organic chemistry, no investigation of the mass spectral behavior of aliphatic aldehydes has as yet been performed using the techniques of isotopic labeling, exact mass measurement, and metastable peak analysis. The present study, utilizing hexanal and all of its possible deuterated analogs as substrates as well as several pertinent labeled heptanals, has shed new light on the electron impact induced behavior of aliphatic aldehydes. Several interesting observations have been made, including the origin of the hydrogen atoms in the loss of water (Tables III and IV), the multiple, and yet not indiscriminate, expulsion of ethylene (Schemes I and II), the apparent nonspecificity of the "McLafferty" rearrangement leading to an ionized olefin (Scheme IV), and the reciprocal hydrogen transfer (Scheme VI) associated with the loss of a propyl radical.

A major program has been initiated in our laboratories directed toward the use of artificial intelligence computer techniques in the interpretation of mass spectra.[4] The first stages of this research program involved the establishment of necessary "rules" for computer-assisted mass spectral interpretation of simple monofunctional compounds, aliphatic ketones having been selected as an initial test case.[4b] Much information is known concerning the electron impact induced fragmentation pathways of ketones,[5] and these data made the successful formulation of rational rules possible. In the course of continuing work, attempts were made to extend these computer techniques to the interpretation of aliphatic aldehyde mass spectra, but it soon became obvious that serious gaps existed in our knowledge concerning the fragmentation patterns of such compounds. Although Gilpin and McLafferty[6] have documented over 10 years ago numerous straight chain aldehyde mass spectra, no high-resolution measurements, low voltage measurements, metastable peak analyses, or isotopic labeling studies have been performed in the intervening years—a surprising state of affairs considering the importance of the aldehyde functionality. Anticipating the results of our study, several earlier assumptions concerning electron impact induced aldehyde fragmentation have now been shown to be erroneous. Other proposed fragmentation mechanisms, formerly based only on speculation, have now been substantiated by experimental evidence.

This work, then, describes a systematic investigation of mass spectral aliphatic aldehyde fragmentation pathways. The powerful techniques of deuterium labeling, high-resolution mass measurement, and defocusing metastable peak determination[7] all proved essential to the achievement of the goals of this project. Hexanal (I) and its six deuterium-labeled analogs were chosen as suitable substrates for preparative considerations and because the chain length seemed sufficiently long so as to be typical of other aliphatic aldehyde systems. Certain deuterium-labeled analogs of heptanal (II) were also synthesized to confirm and clarify several results initially observed in the mass spectra of the labeled hexanals.

Discussion of Results

The mass spectra at 70 eV and at nominal 12 eV of hexanal (Figures 1 and 2) and heptanal (Figures 3 and 4) are reproduced. Only a very weak molecular ion is observed for each aldehyde, even at low voltage. In the mass spectrum of hexanal an M − 1 ion (*m/e* 99) is present but its abundance is small (less than one-half that of the molecular ion), and a pressure-dependent M + 1 ion (*m/e* 101) can also be observed. Two very prominent peaks, *m/e* 44 and *m/e* 56, are seen at high voltage. It should be noted that while the *m/e* 44 peak (associated with a McLafferty rearrangement[5])

(1) For paper CLXXXII, see R. T. Gray and C. Djerassi, *J. Org. Chem.*, in press.

(2) Financial support from the National Institutes of Health (Grant No. AM-04257) is gratefully acknowledged. The purchase of the CH-4 mass spectrometer was made possible by NASA (Grant No. NGR-05-020-004).

(3) National Institutes of Health Predoctoral Fellow.

(4) (a) J. Lederberg, G. L. Sutherland, B. G. Buchanan, E. A. Feigenbaum, A. V. Robertson, A. M. Duffield, and C. Djerassi, *J. Am. Chem. Soc.*, 91, 2973 (1969); (b) A. M. Duffield, A. V. Robertson, C. Djerassi, G. L. Sutherland, E. A. Feigenbaum, and J. Lederberg, *ibid.*, **91**, 2977 (1969); (c) G. Schroll, A. M. Duffield, C. Djerassi, B. G. Buchanan, G. L. Sutherland, E. A. Feigenbaum, and J. Lederberg, *ibid.*, in press.

(5) For a detailed and up to date coverage see H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1967, Chapter 3.

(6) J. A. Gilpin and F. W. McLafferty, *Anal. Chem.*, **29**, 990 (1957).

(7) (a) K. R. Jennings, "Some Newer Physical Methods in Structural Chemistry," R. Bonnett and J. G. Davies, Ed., United Trade Press, London, 1967, p 105; (b) T. W. Shannon, T. E. Mead, C. G. Warner, and F. W. McLafferty, *Anal. Chem.*, **39**, 1748 (1967).