Tetrahedron, 1966, Vol. 22, pp. 3093 to 3101. Pergamon Press Ltd. Printed in Northern Ireland

CHARACTERIZATION OF UNSATURATED HYDROCARBONS BY MASS SPECTROMETRY[1]

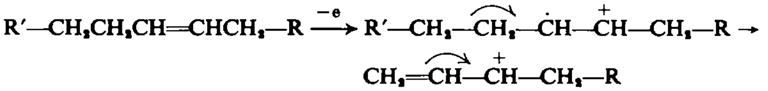
R. E. WOLFF,[2] GENEVIEVE WOLFF[2] and J. A. McCLOSKEY

Department of Biochemistry, Baylor University College of Medicine, Houston, Texas

(*Received* 22 *March* 1966)

Abstract—The mass spectra of O-isopropylidene derivatives of diols obtained by stereospecific oxidation of a number of long chain olefins are interpreted, and are shown to be useful for the characterization of both positional and geometrical isomers.

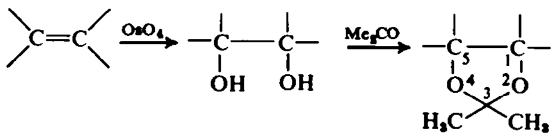
MASS spectrometry has evolved as a highly useful tool in the structural characterization of long chain compounds, principally esters[3] and hydrocarbons.[4] In considering those structural features[5] which on electron impact lead to the formation of well-stabilized carbonium ions, cleavage of a carbon–carbon bond beta to a double bond seemingly represents one of the most favorable processes in the realm of simple cleavages:



$$R'{-}CH_2CH_2CH{=}CHCH_2{-}R \xrightarrow{-e} R'{-}CH_2{-}CH_2{-}\dot{C}H{-}\overset{+}{C}H{-}CH_2{-}R \rightarrow CH_2{=}CH{-}\overset{+}{C}H{-}CH_2{-}R$$

However, the identity or great similarity of mass spectra of geometrical and positional isomers of olefins attests to the inability of mass spectrometry to determine double bond positions and configurations, unless the double bond is in close proximity to another functional group. This has been generally attributed[6] to extensive and facile hydrogen rearrangement (i.e., double bond migration) along the chain after molecular ion formation and before fragmentation.

A recent approach to this problem in the case of unsaturated fatty esters[7] has been the stereospecific oxidation of the double bond to a vicinal diol, followed by condensation with acetone to yield the corresponding O-isopropylidene derivative:



---

[1] Presented in part at the Mass Spectroscopy Group Conference, London, September, 1965.

[2] Present address: Institut de Chimie, Université de Strasbourg, Strasbourg, France.

[3] R. Ryhage and E. Stenhagen in *Mass Spectrometry of Organic Ions* (Edited by F. W. McLafferty) Chap. 9. Academic Press, New York (1963).

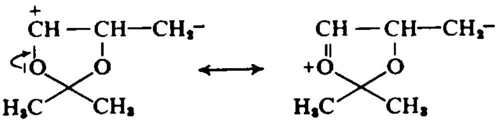
[4] M. J. O'Neal and T. P. Wier, *Analyt. Chem.* **23**, 830 (1951).

[5] See for instance, K. Biemann, *Mass Spectrometry*, Chap. 3. McGraw-Hill, New York (1962).

[6] Ref. 5, p. 83.

[7] J. A. McCloskey and M. J. McClelland, *J. Amer. Chem. Soc.* **87**, 5090 (1965).

We have extended this approach to a simpler and more general system, that of unsaturated hydrocarbons, with two expectations. First, the absence of the carbomethoxy group, which plays a considerable role in the formation of ions in the case of the esters, would result in relatively simpler mass spectra, which would facilitate location of the 1,3-dioxolane ring through ions formed by cleavage alpha to the ring:



Second, the absence of other interacting functional groups in the chain might result in quantitatively predictable variations in intensity as a function of stereochemistry. Both of these expectations have been borne out to a considerable extent, as will be discussed.

The procedure for conversion of olefins to O-isopropylidene derivatives is well suited for mass spectrometry since the reactions are quantitative and easily carried out on a milligram scale. In addition, the use of a stereospecific oxidant such as OsO_4 (*cis*-specific) results in isomerically pure products which bear a direct relationship to the olefin in a stereochemical sense: e.g., *cis*-olefin → *erythro*-diol → *cis*-O-isopropylidene derivative (*cis*-2,2-dimethyl-4,5-dialkyl-1,3-dioxolane). The use of acetone for the condensation reaction offers two advantages. First, the *cis* and *trans* isomers of the resulting O-isopropylidene derivatives of both esters and hydrocarbons may be separated gas chromatographically on non-polar phases (e.g., SE-30), which may be quite useful either alone or with mass spectrometers employing gas chromatographic inlet systems. Second, the ready availability of d_6-acetone allows the easy preparation of the corresponding hexadeuterio derivatives. These labelled compounds are quite useful for unambiguously establishing the location of the dioxolane ring in the chain, as will be discussed. Use of the deuterated analogs as well as O^{18}-labelled derivatives (obtained via $OsO_4{}^{18}$)[7] have also aided in corroboration of proposed modes of fragmentation.

In contrast to the corresponding long chain esters, mass spectra of O-isopropylidene derivatives of olefins exhibit relatively simple mass spectra. The mass spectrum of

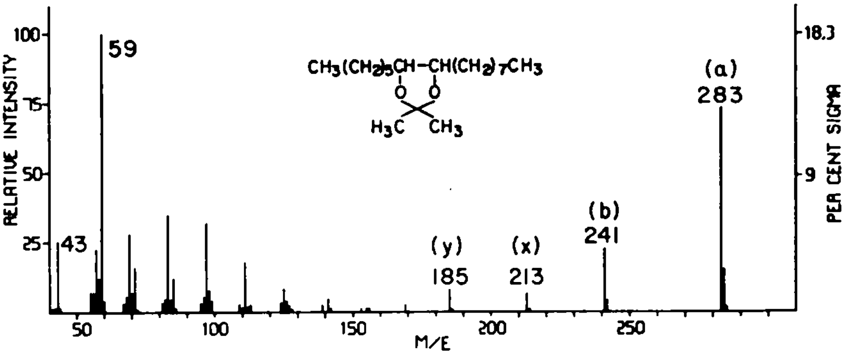
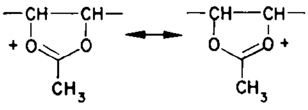


Fig. 1. Mass spectrum of the O-isopropylidene derived from *cis*-7-hexadecene.

cis-O-isopropylidene-7,8-dihydroxyhexadecane (I, Fig. 1) derived from *cis*-7-hexadecene, serves as a typical representative of the compounds studied. As in corresponding derivatives of carbohydrates[8] and fatty esters,[7] the molecular weight is clearly indicated in every case by an intense peak at M-15 (*m*/*e* 283, ion *a*, Fig. 1), due to loss of a methyl group from the dioxolane ring, giving rise to a highly stabilized tertiary carbonium ion:



a (M-15)

Loss of 18 mass units (CD_3) thus occurs from the hexadeuterio analog (II, Fig. 2). Further elimination of ketene (42 and 44 mass units in I and II, respectively) results in a protonated epoxonium ion *b* (*m*/*e* 241), or its labelled analog (*m*/*e* 242), as previously[7] postulated:

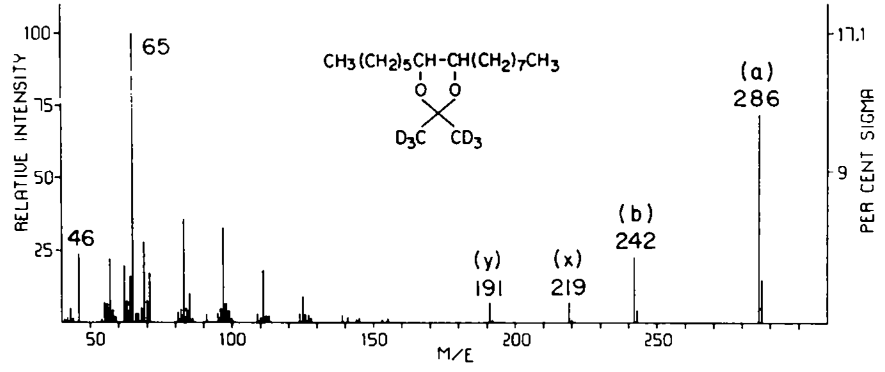


FIG. 2. Mass spectrum of the d_6-O-isopropylidene derived from *cis*-7-hexadecene.

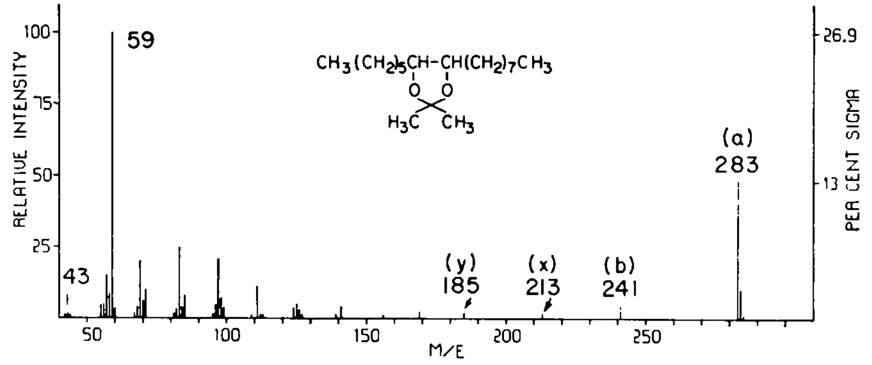
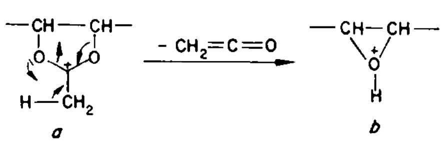


FIG. 3. Mass spectrum of the O-isopropylidene derived from *trans*-7-hexadecene.



a *b*

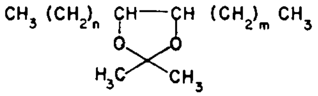
---

[8] D. C. De Jongh and K. Biemann, J. *Amer. Chem. Soc.* **86**, 67 (1964).

Conspicuous in its absence is the elimination of acetic acid from ion *a*, which in the corresponding esters represents a second major path of decomposition. Since the mechanism postulated for this process[7] involved hydrogen alpha to the dioxolane ring, and was therefore not directly related to the presence of the carbomethoxy group, its absence in the hydrocarbon derivatives was somewhat unexpected.[9]

The most intense peak in every case studied, *m/e* 59, is due to the elements of protonated acetone (d_6-acetone, *m/e* 65 in Fig. 2). A recurring group of hydrocarbon peaks occurs every 14 mass units, the majority of which are alkene ions (*m/e* 69, 83, 97, 111, etc.), and play no significant structural role in interpretation of the spectra.

The position of the dioxolane ring (and hence the original double bond) in the chain is indicated by simple bond cleavages alpha to the dioxolane ring. The resulting secondary carbonium ions (e.g., *x* and *y* in Fig. 1) are stabilized by one of the adjacent ether oxygens.[10] Identification of these peaks is facilitated in several ways. For the general case



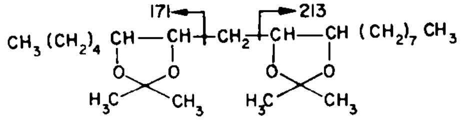
the mass values of the two ions are restricted to 101 + 14(n + 1) and 101 + 14(m + 1). In addition, their sum minus 100 equals the molecular weight. Also, the routine use of d_6-acetone in the condensation reaction provides an easily recognized shift of six mass units due to the presence of two trideuteriomethyl groups on the dioxolane ring. Thus *m/e* 185 (*y*) and 213 (*x*) in Fig. 1 shift clearly to *m/e* 191 and 219 in Fig. 2. In the case of O-isopropylidenes derived from 5-alkenes, ions *x* and *b* will occur at the same nominal mass, M-57. These ions may be separated by either high resolution measurements (2 oxygens vs. 1), or deuterium labelling. Thus in the spectrum of the O-isopropylidene from 5-eicosene (Fig. 8), *m/e* 297 was found to consist of approximately 80% *b* and 20% *x* as determined from *m/e* 298 and 303 in the spectrum of the d_6 analog.

Another convenient form of labelling may in effect be employed by condensation of the diol with acetaldehyde rather than acetone. For example, the 2-methyl-1,3-dioxolane (see Fig. 4) derived from *cis*-7-hexadecene contains one less methyl group on the dioxolane ring, giving rise to α-cleavage peaks which shift fourteen mass units lower when compared with the corresponding acetone condensation product. Thus *m/e* 185 and 213 in Fig. 1 shift to *m/e* 171 and 199 in Fig. 4. Although the α-cleavage peaks and hydrocarbon peaks at lower mass in Fig. 4 appear relatively more intense, they carry approximately the same percentage of total ion current as their counterparts in Fig. 1. In the upper mass range of Fig. 4, loss of a methyl radical from M results in a well-stabilized secondary carbonium ion at *m/e* 269. Loss of hydrogen from

---

[9] As a result of this observation deuterium labeling experiments are currently in progress to determine the mechanistic origin of the hydrogen involved in the *a*–CH_2CO_2H process in the ester derivatives.

[10] It is of interest to note that in the mass spectrum of the di-O-isopropylidene derived from 6,9-octadecadiene, only two of the four possible ions arising from α-cleavage are observed–*m/e* 171 and 213 (*m/e* 177 and 219 in the d_{12}-analog):



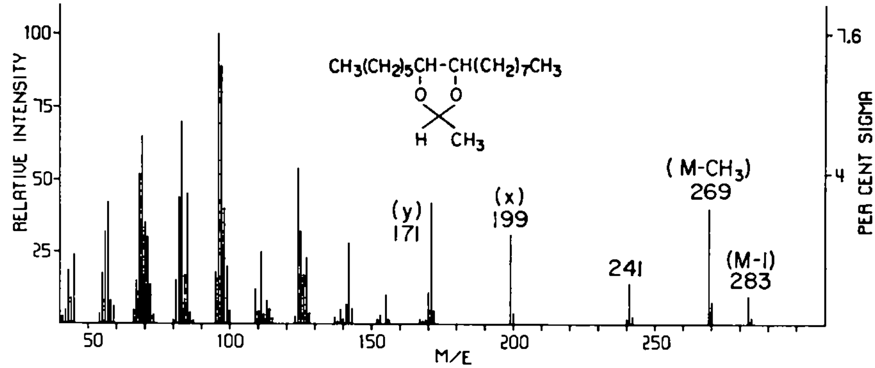


FIG. 4. Mass spectrum of *cis*-2-methyl-4-hexyl-5-octyl-1,3-dioxolane from *cis*-7-hexadecene.

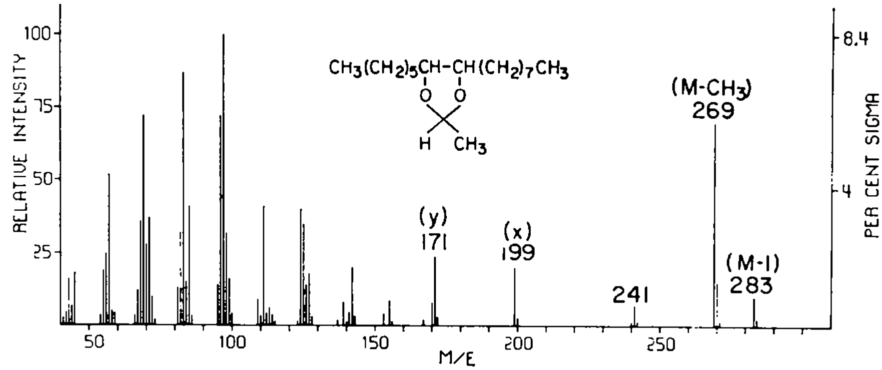


FIG. 5. Mass spectrum of *trans*-2-methyl-4-hexyl-5-octyl-1,3-dioxolane from *trans*-7-hexadecene.

C-2 of the dioxolane ring yields *m/e* 283, which is structurally, although perhaps not energetically, the same as ion *a* in Fig. 1. The expected further loss of ketene then yields *m/e* 241. Although the loss of hydrogen results in a slightly more stable (tertiary) ion than that formed by loss of the methyl group (secondary), the fourfold greater intensity of M-15 in Fig. 4 appears to reflect the more energetically favourable loss of the methyl radical over the hydrogen radical.

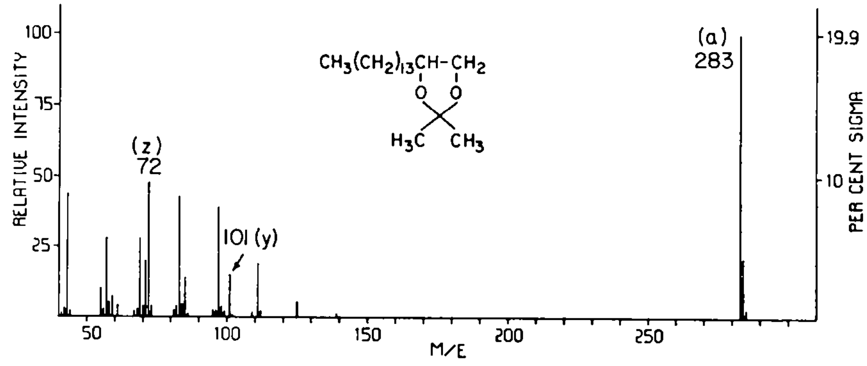
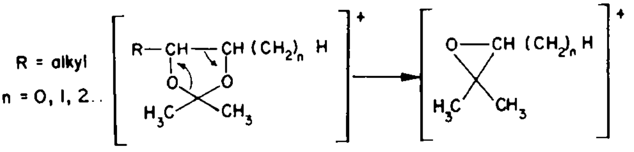


FIG. 6. Mass spectrum of the O-isopropylidene derived from 1-hexadecene.

For O-isopropylidenes derived from olefins in which the double bond is not near a terminal position, only the α-cleavage peaks and *m/e* 59 shift six mass units in the labelled analogs. However, in cases in which the dioxolane ring is moved closer to the terminal position, another fragment ion containing both methyl groups attached to C-2 of the ring becomes evident, and increases in intensity. The extreme example is *m/e* 72 (*z*) in spectra of O-isopropylidenes derived from 1-alkenes such as 1-hexadecene (Fig. 6). O^{18} labelling reveals the presence of one dioxolane ring oxygen, thus also requiring retention of the tertiary carbon atom of the ring, and the carbon atom of the chain which bears the smallest hydrocarbon substituent:[11]



The formation of this ion (arbitrarily indicated above as an epoxide) thus appears to be a sensitive indicator of the proximity of the ring to the end of the chain. In addition to its six mass unit shift in the d_6-derivatives, ions of this type may be recognized by their occurrence twenty nine mass units below ion *y*, at *m/e* 72 + n (14), where n is an

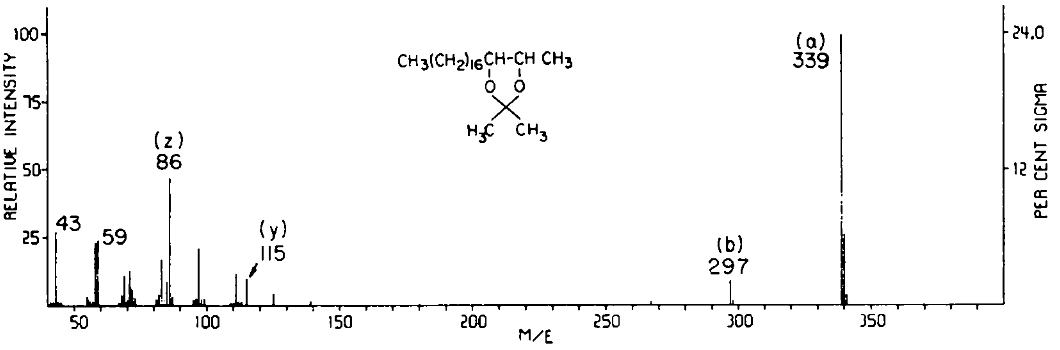


FIG. 7. Mass spectrum of the O-isopropylidene derived from *cis*-2-eicosene.

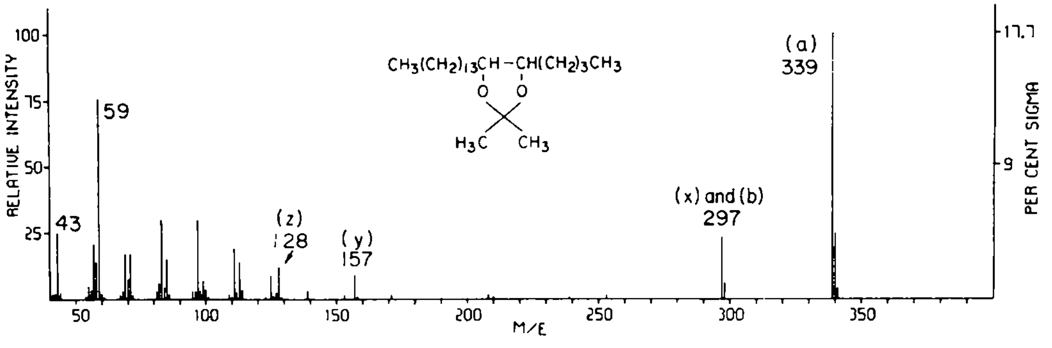


FIG. 8. Mass spectrum of the O-isopropylidene derived from *cis*-5-eicosene.

---

[11] This reasoning is validated by the presence of *m/e* 72 as an intense peak in the mass spectrum of the O-isopropylidene from methyl ω-undecenoate (unpublished results of M. J. McClelland).

integer. This ion is thus observed at *m/e* 86 in derivatives of 2-alkenes, such as 2-eicosene (Fig. 7). When shifted to the 5-position *z* is of low abundance (see Fig. 8) but still evident (from deuterium labelling), and is virtually absent in Figs. 1 (*m/e* 156 and 2 (*m/e* 162, not shown).

The influence of stereochemistry on the mass spectra of both the acetone and acetaldehyde condensation products is evident from a comparison of spectra of the *cis* and *trans* isomers[12] in Figs. 1 and 3, and 4 and 5, respectively, which indicate, as in the case of the O-isopropylidenes of unsaturated esters,[7] consistent, marked, intensity variations as a function of stereochemistry. But to a certain extent unlike the esters the abundance relationship between diastereoisomers appears to be relatively constant and unaffected by positional isomerism. Table 1 lists the calculated *cis* to *trans* ratios

TABLE 1. COMPARISONS OF PER CENT TOTAL IONIZATION OF SEVERAL IONS FROM THE MASS SPECTRA OF O-ISOPROPYLIDENES DERIVED FROM LONG CHAIN UNSATURATED HYDROCARBONS

Hydrocarbon	Mass Spectrum Figure	$\%\Sigma_{40}$	Ion *b* $\%\Sigma$ *cis*/$\%\Sigma$ *trans*	$\%\Sigma$ *cis*/$\%\Sigma$ *trans* for ions *x* and *y*; ($x > y$) *x*	*y*
cis-2-eicosene	7	2·09	4·2	—	2·3
trans-2-eicosene		0·50			
cis-5-eicosene	8	3·58	3·9	2·3	2·6
trans-5-eicosene		0·93			
cis-7-hexadecene	1	4·44	3·8	2·6	2·7
trans-7-hexadecene	3	1·16			
cis-9-octadecene	9	3·79	3·9$_6$	2·7*	
trans-9-octadecene		0·96			
cis-9-docosene	10	3·22	3·8	2·6	2·6
trans-9-docosene		0·85			

* Ions *x* and *y* are indistinguishable since the molecule is symmetrical.

of $\%\Sigma$ of several ions from five pairs of compounds. The positions of the dioxolane ring vary from the center of the chain to the most extreme position (2, 3) for which isomerism is possible, with chain lengths from C-16 to C-22. Considering the M-15-42 ions (*b*), it is evident that $\%\Sigma$ for *cis* isomers varies from about 2 to 4%. However, direct comparison of isomers of each compound, measured as the $\%\Sigma$ ratios of *cis* to *trans*, are remarkably constant at about 3·9, with the greatest variation shown, not unexpectedly, from the molecule in which the ring is in an extreme position.

Applying the same calculations to the alpha cleavage ions *x* and *y* results in another relatively constant set of ratios of about 2·6. The greater ease with which ions *x* and *y* are formed from *cis*-isomers may be attributed to the relatively greater relief of steric

---

[12] It should be pointed out that condensation of the diols with acetaldehyde instead of acetone generates an additional asymmetric carbon at C-2 of the dioxolane ring. The acetaldehyde derivatives are therefore mixtures of two stereoisomers. Some of the intensity differences between Figs. 4 and 5 therefore must be attributed to some (indeterminate) extent to the presence of these isomers.

hindrance which exists between the alkyl side chains of the dioxolane ring when one of these groups is lost. In the case of the O-isopropylidenes derived from the 2-eicosene isomers, the formation of ion x (as distinct from ion a, both M-CH_3) is negligible, as shown by the exclusive loss of CD_3 in the case of the hexadeuterio analogs. This may be attributed to the greater stability of the tertiary carbonium ion (two adjacent oxygen atoms) resulting from loss of a ring methyl, as opposed to the secondary ion (one adjacent oxygen) resulting from loss of the chain methyl.

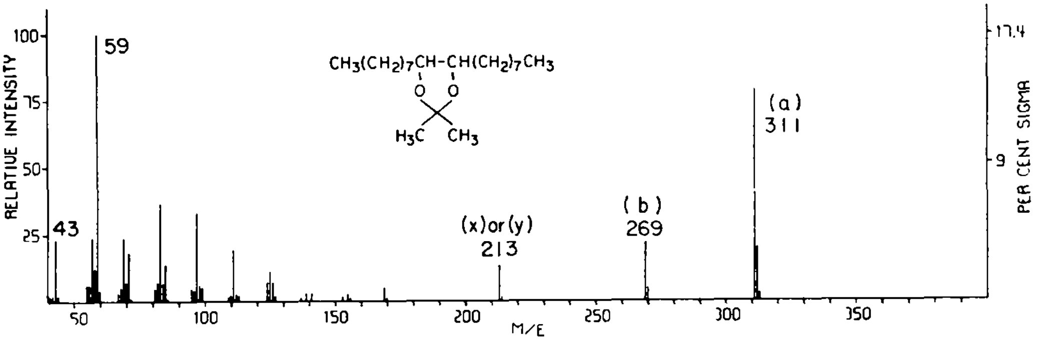


FIG. 9. Mass spectrum of the O-isopropylidene derived from *cis*-9-octadecene.

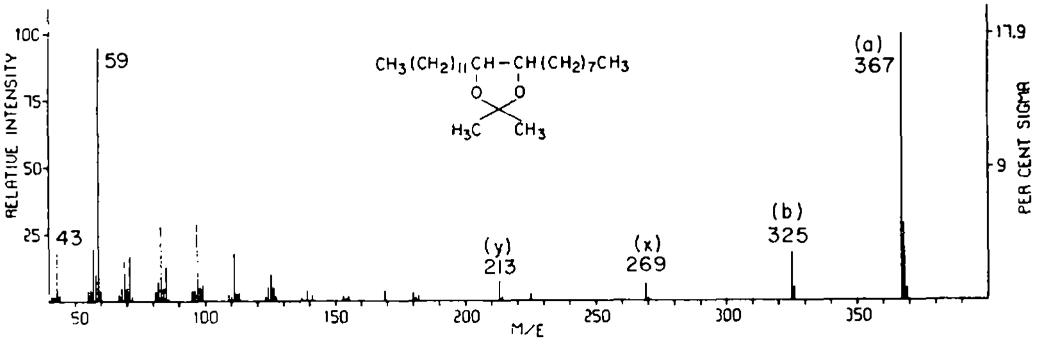


FIG. 10. Mass spectrum of the O-isopropylidene derived from *cis*-9-docosene.

EXPERIMENTAL

Mass spectra were determined with an Atlas–Werke CH-4 mass spectrometer, equipped with a gas chromatographic (1% SE-30, 115–175°) inlet system.[13] The transfer system (including He separators) was maintained at 170° and the ion source 250°. Ionizing potential was 20 ev; ionizing current 60 μa; ion source pressure, $\sim 2 \times 10^{-6}$ mm. Spectra from 1–10 μg samples were recorded in 4–6 sec on the apex of the gas chromatographic peak, as indicated by the gas chromatogram continously produced by a total ionization monitor.

Unsaturated hydrocarbons. Samples of 1-hexadecene and 1-octadecene were obtained commercially. 2-Eicosene was prepared as a *cis*-rich mixture of the *cis* and *trans* isomers by the Wittig reaction between octadecyl-1 triphenylphosphonium bromide and acetaldehyde.[14] The remaining hydrocarbons were prepared from the corresponding unsaturated esters by $LiAlH_4$

---

[13] R. Ryhage, *Analyt. Chem.* **36**, 759 (1964).

[14] C. F. Hauser, T. W. Brooks, M. L. Miles, M. A. Raymond and G. B. Butler, *J. Org. Chem.* **28**, 372 (1963).

reduction to the alcohols, followed by reduction of the tosylates.[15] Location and stereochemistry of double bonds are unaffected by this latter procedure. *trans*-Hydrocarbons not derived directly from *trans*-esters were obtained by isomerization of the *cis*-hydrocarbon by heating 6 hr with Se in a sealed tube at 200–225°. Under these conditions essentially no migration of the double bond occurs[16] and a mixture of geometrical isomers results. The corresponding O-isopropylidenes were well separated in the gas chromatographic inlet of the mass spectrometer. The *trans*-derivative had a shorter retention time than its *cis*-isomer in every case studied.

Preparation of OsO_4[18] has been previously reported.[7]

O-*Isopropylidene derivatives* were prepared by a procedure similar to those previously employed.[7,17] To 1 mg of the hydrocarbon was added 0·2 ml pyridine–dioxane mixture (1:8), followed by 0·1 ml dioxane containing 1 mg OsO_4. After standing 2 hr, addition was made of 6 ml of a freshly prepared Na_2SO_3 suspension made by addition of 1·5 ml freshly prepared 16% Na_2SO_3 to 5 ml MeOH. After 1 hr the mixture was centrifuged, the supernatant evaporated to dryness under red. press., redissolved in ether and evaporated to dryness. The resulting diol was condensed with 0·1–0·5 ml acetone (or acetaldehyde for the preparation of 2-methyl-4,5-dialkyl-1,3-dioxolanes) or 0·2–0·3 ml d_6-acetone, in the presence of 50 mg $CuSO_4$ upon heating 1 hr at 50° in a tightly sealed tube. The reaction mixtures were injected directly on the gas chromatographic column connected to the mass spectrometer.

Acknowledgment—We are indebted for support of this work through grants from the National Institutes of Health (He-05435) and the Robert A. Welch Foundation (Q-125).

[15] H. Schmidt and P. Karrer, *Helv. Chim. Acta.* **32,** 1371 (1949); L. L. Gelb, W. S. Port and W. C. Ault, *J. Org. Chem.* **23,** 2022 (1958).

[16] J. J. A. Blekkingh, H. J. J. Janssen and J. G. Keppler, *Rec. trav. chim.* **76,** 35 (1957).

[17] K. Tanaka and E. C. Horning, to be published.