tation[15] of octahedral coördination. The structure of the blue form of the compound has not been deciphered but it is isomorphous with the corresponding bromide and iodide[14] for which only blue forms are known. The hypothesis that these are tetrahedral rather than octahedral cobalt structures, based on the correspondence of the spectra of the solid and the entity in solution, seems reasonable.

Cobaltous chloride monohydrate is a blue-violet solid, whose absorption parallels roughly that of the "violet" forms above, but combines the two peaks of the latter in a single broad absorption. The flat maximum in the absorption comes at about 560 mμ. Anhydrous cobaltous chloride (in the presence of calcium sulfate, to maintain its anhydrous state) has a principal peak at about 600 mμ, with a suggestion of structure in the region from 640–690 mμ. A minor peak is indicated about 535 mμ. The color is a very pale blue, compared to the rich blue of the salts with the $CoCl_4^=$ grouping. Crystallographic investigation has assigned the solid the $CdCl_2$ structure,[16] with the cobalt being 6-coördinate. It seems reasonable to conclude, therefore, that the spectra of the anhydrous chloride and of the monohydrate represent further extension of the difference between the violet dihydrate or dipyridinate and the hexahydrated or hexapyridinated forms, and that the spectral shift leading to visual blueness may be ascribed to the mass effect of coördination predominately to chloride rather than oxygen or nitrogen. An analogous shift of spectrum to longer wave lengths is seen on comparing the spectra of solutions of cobalt chloride, bromide and iodide in the respective hydrogen halide acids.[9]

In the case of glasses, pigments, etc., in which cobalt is a minor component, it has already been proposed that the blue or red color of the substance is correlated with the 4-coördination or the 6-coördination of the basic lattice structure.[17-20] In summary, therefore, one may say that the Co(II) solids which are red or pink certainly have 6-coördinate cobalt; the violet forms of the composition $CoX_2 \cdot 2S$ (X = halide, S = molecular base) are most probably all 6-coördinate also; and most of the blue forms are 4-coördinate. The exceptions to the last are blue solids in which 6-coördinate cobalt is attached predominately to heavy atoms, such as Cl and heavier. In the case of the violet $CoX_2 \cdot 2S$ forms it does not seem too likely that the secondary long wave length peak signalizes the presence of two kinds of cobalt atoms in the solids, with some small proportion (perhaps just at the crystal surface) coördinated to only 4 groups. The more probable explanation is that the secondary peak represents a displacement of one of the peaklets not so well resolved in the hexapyridinate spectrum.

Added Note.—Since the above report was written, it has been possible to prepare a sample of Cs_2CoCl_4 in a non-absorbing matrix for transmission measurements at considerably higher resolution than was possible for the reflection spectra. This material, observed both at room temperature and at liquid nitrogen temperature, shows a wealth of structural details otherwise unobserved, and will be the subject of a separate report.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BROOKHAVEN NATIONAL LABORATORY, AND THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Mass Spectra of Six Lactones[1]

BY LEWIS FRIEDMAN AND F. A. LONG

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Mass spectra are given for the aliphatic lactones, β-propio, γ-butyro, γ-valero, γ-crotono, β-angelica and α-angelica. For four of the lactones spectra were also obtained of samples with carbonyl oxygens containing enriched O^{18}. A detailed discussion of the data is given and it is concluded that the main peaks of the spectra result from splitting of two alternate bonds of the lactone rings. The stability of the parent molecule ions is greater with the unsaturated lactones and their spectra are characterized by larger intensity of peaks due to rearrangement. Although there are frequent large variations in yields of particular ions, the spectra for both the saturated and the unsaturated lactones arise from similar bond splitting processes.

This paper gives the mass spectra of six simple aliphatic lactones, three saturated and three unsaturated. Five of the lactones are five-membered rings and one, β-propiolactone, is a four-membered ring. Figure 1 gives the structures of the six lactones. The ring bonds are numbered for convenience in later discussions.

The mass spectral data have been examined in some detail from the standpoint of the most probable ion dissociation processes. This approach has led to fairly definite conclusions about the origins of the majority of the peaks and to a good qualitative correlation of spectra with molecular structure. A further object of this study was to provide knowledge for interpretation of the mass spectrum of diketene; this problem will be considered in a subsequent communication.

Experimental

Materials and Procedure.—The mass spectrometer analyses were made using a General Electric mass spectrometer. Spectra were scanned magnetically using 2000 v. ion accelerating potential and an electron accelerating potential of 50 v. Mass assignments were made independently using H_2O^+, CO_2^+ and the Hg^{++} background in the machine as

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[1] Research carried out under the auspices of the Atomic Energy Commission.

interval standards combined with careful measurement of ion accelerating voltages at constant magnetic field. The voltage measurements were made through a 500 megohm dividing network with a Leeds and Northrup type K potentiometer and a galvanometer having a sensitivity of 5 × 10^{-3} ma./mm. The high resistance network was devised to eliminate any appreciable lowering of the resistance in the high voltage potentiometer of the mass spectrometer. Precision of mass identification was generally ±0.1 mass unit over a limited mass range.

The β-propiolactone was obtained from the B. F. Goodrich Company, the γ-butyrolactone from the Clifts Dow Company and the γ-valerolactone from the Monsanto Chemical Company. All of these were dried and redistilled under reduced pressure. Refractive index and titration tests showed them to be at least 99% pure.

The angelica lactones were obtained from the Chemical Procurement Company. The refractive indices were $n^{25}\mathrm{D}$ 1.4435 for the α-angelicalactone and $n^{25}\mathrm{D}$ 1.4516 for the β-angelicalactone. The α-angelicalactone had a melting point of 18°.

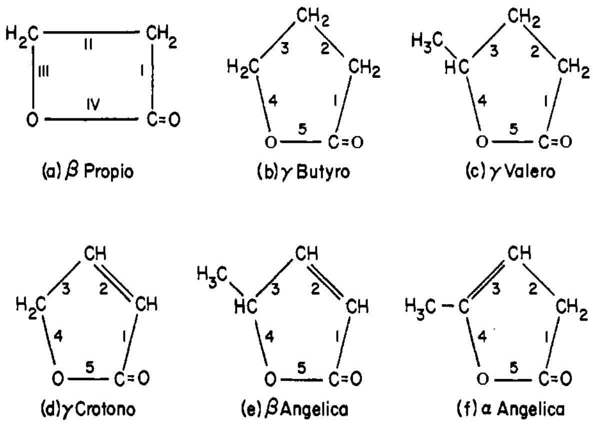
The lactone of γ-hydroxyisocrotonic acid was prepared by the method of Glattfield, Leavell, Spietts and Hulton.[2] The refractive index was $n^{20}\mathrm{D}$ 1.4671 and the b.p. was 70° at 3.0 mm.

Three of the lactones were equilibrated in water containing 1.5% O^{18} in order to label the carbonyl oxygen. The procedures were similar to those used previously with γ-butyrolactone.[3] Three ml. of the γ-valerolactone was added to 11 ml. of a solution of 1 *M* sulfuric acid in H_2O^{18} (1.5% O^{18}) and the solution was permitted to stand at elevated temperature for a time calculated to be ample for the carbonyl oxygen of the lactone to equilibrate with the enriched water. A similar labeling of the carbonyl oxygens was done with two of the unsaturated lactones but for these the hydrolysis was done in basic solution, since the rates and equilibria of the acid-catalyzed hydrolysis were not known. In each case 2 ml. of the lactone was added to 10 ml. of 1 *M* sodium hydroxide in enriched water (1.5% O^{18}) and the solution was later acidified with concentrated sulfuric acid to re-form the lactone. In all cases the lactones were ultimately extracted with benzene and recovered by distillation. Since both the hydrolysis and subsequent re-formation of γ-lactones involve reaction only of the acyl–oxygen bond,[3] the final lactones will contain enriched oxygen only in the carbonyl oxygen, *i.e.*, the hydroxyl oxygen will not be affected.

Experimental Results

The mass spectra of the six lactones are given in Table I. The relative ion intensities are normalized on the basis of 100 for the most intense peak; peaks with intensity below unity are omitted in the tabulations except in one special case. Since for some purposes comparison in terms of total ion yield are useful, these are given in the bottom row of Table I.[4]

Mass spectral patterns were also obtained for three of the lactones, γ-valero, γ-crotono- and β-angelicalactone, labeled with approximately 1.5% of O^{18} in the carbonyl oxygen. In line with the small enrichment of the oxygen the over-all patterns are very close to those of the ordinary lactones, the only significant differences occurring at the "isotopic" peaks (peaks for masses two higher than normal, corresponding to the presence of O^{18} rather than O^{16}). Table II gives the observed intensity ratios of the isotopic and normal peaks for the ordinary and enriched lactones and also gives the earlier data for γ-butyrolactone.[3] Data are given only for masses where the O^{18} peaks are comparatively free from interferences from other normal peaks or from background. In calculating the ratios of Table II no corrections have been made for background, C^{13} contributions, etc.


(a) β Propio (b) γ Butyro (c) γ Valero

(d) γ Crotono (e) β Angelica (f) α Angelica

Fig. 1.—Formulas for lactones.

The ratios shown in Table II for the parent peaks for all four lactones show, as expected, that in the labeled molecules only one oxygen is enriched and from the earlier discussion this must be the carbonyl oxygen. More detailed calculations show that for the enriched samples of γ-butyro-, γ-valero- and γ-crotonolactones essentially complete exchange of the carbonyl oxygen has occurred. The data imply somewhat less than complete exchange for the β-angelicalactone carbonyl oxygen although this may only be lack of precision in the measurement of peak heights. Since the 83 peak in β-angelicalactone undoubtedly results from the loss of the side chain methyl group, the observed 85/83 ratios simply confirm the results from the parent ion ratios; a similar conclusion holds for 87/85 ratios for γ-valerolactone.

The 31/29 and 30/28 ratios in the γ-valerolactone spectra are essentially the same for the "enriched" and "ordinary" samples. Similar results were obtained with γ-butyrolactone indicating that for both of these molecules the ions of mass 28 and 29 do not contain the carbonyl oxygen, *i.e.*, that a 1–5 split does not occur. Conceivably the 28 and 29 peaks could be CO^+ and HCO^+ from dissociation of H_2CO^+ of mass 30 after a 3–5 split. Actually the mass 30 peaks for these lactones are very low and can be explained as being C^{13} "isotopic" peaks for $C_2H_5^+$. We thus conclude that the observed peaks at mass 28 and 29 are very probably due to the ions $C_2H_4^+$ and $C_2H_5^+$.

For γ-butyrolactone the 58/56 ratios of Table II show that essentially all of the mass 56 ions contain the carbonyl oxygen. This clearly indicates a 3–5 split to give the ion $C_3H_4O^+$. With the γ-valerolactone a detailed comparison of the 58/56 ratios with those for 87/85 (which are more accurate than the parent ion ratios) reveals that only approximately half of the mass 56 ions contain the carbonyl oxygen. The explanation of this is almost certainly that part of the intensity at mass 56 arises from the $C_4H_8^+$ ion formed by a 1–4 split.

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[2] J. W. E. Glattfield, G. Leavell, G. E. Spietts and D. Hulton, THIS JOURNAL, **53**, 3164 (1931).

[3] F. A. Long and L. Friedman, *ibid.*, **72**, 3692 (1950).

[4] It should be pointed out that accurate determination of sensitivity coefficients for these relatively non-volatile molecules was not possible in our experimental arrangement so that intercomparisons of total ion yields are implicitly based on an assumption of constant total ions for these fairly similar molecules under fixed instrumental conditions. See also F. L. Mohler, L. Williamson and H. M. Dean, *J. Research Natl. Bur. Standards*, **42**, 235 (1950).

TABLE I

MASS SPECTRA OF LACTONES

m/e	β-Propio	γ-Butyro	γ-Valero	γ-Crotono	β-Angelica	α-Angelica	Fragments
14	20.1	4.6	5.0	...	4.3	6.2	CH_2
15	30.5	4.6	11.2	...	15	18.3	CH_3
18	2.9	6.2	18.3				
26	16.5	15.6	14.9	41	33	19.6	C_2H_2
27	11.8	33.9	35.4	64	54	51	C_2H_3
28	64.2	100.0	94.7	24	29.6	21	C_2H_4; CO
29	19.2	37.9	63.3	21	15	3	HCO; C_2H_5
36				1	4	1	C_3
37		2.9		7	3	3	C_3H
38		3.9		9	3	4	C_3H_2
39		12.4	16.1	20	17.4	15.7	C_3H_3
40		9.4	4.4				
41	4.0	41.2	52.0	2	8.5	6.2	C_2HO; C_3H_5
42	100.0	85.7	7.9	0.3	10.3	15.4	C_2H_2O; C_3H_6
43	31.7	4.9	39.8	1	78	85.3	C_2H_3O
44	5.5	1.4	4.6	16.5	2	8.7	CO_2; C_2H_4O
45			8.3				
46			5.1				
53				44	8.1	6.4	C_3HO; C_4H_5
54				24.6	21	5.5	C_3H_2O; C_4H_6
55	1.8	5.8	9.8	*100*	*100*	*100*	C_3H_3O
56		22.5	*100*	3.7	6.1	3.9	C_3H_4O
57		5.4	21.4				
69				...	8.9	3.5	C_4H_5O; C_3HO_2
70				...	4.7	7.5	C_4H_6O; $C_3H_6O_2$
72							
82				...	...	1.8	$C_4H_2O_2$
83				1.8	32.2	1.5	$C_4H_3O_2$
84				P 51.3	...	...	
85		6.0	41.7				
86		P 20.6	1.9				
88							
98					P 63.4	P 71.7	
99			2.4				
100			P 5.45				
Total ion yield	309	427	562	432	521	460	

TABLE II

PEAK INTENSITY RATIOS FOR NORMAL AND O^{18}-LABELED LACTONES

Lactone	Peaks	Obs. intensity ratios × 10^2 Ordinary	O^{18}-labeled
γ-Butyro	88/86	0.65	1.85
γ-Butyro	58/56	0.97	2.18
γ-Butyro	31/29	6.57	6.79
γ-Butyro	30/28	2.11	1.82
γ-Valero	102/100	0.4[a]	1.3[a]
γ-Valero	87/85	0.40	1.50
γ-Valero	58/56	0.68	1.35
γ-Valero	31/29	2.0	1.97
	30/28	1.50	1.30
γ-Crotono	86/84	0.51	1.57
γ-Crotono	57/55	.48	1.6
β-Angelica	100/98	.64[b]	1.45[b]
β-Angelica	85/83	.9	2.3
β-Angelica	57/55	.56	1.40

[a] Lower accuracy because of lower peak intensity, see Table I. [b] Values obtained with 25 v. ionizing voltage to minimize background from Hg^{++}.

The remainder results from a 3–5 split just as with the γ-butyrolactone.

The observed 57/55 ratios for the two unsaturated lactones show clearly that the 55 fragments contain the carbonyl oxygen. It can be seen in Fig. 1 that this must mean a 3–5 split of the lactone rings with an accompanying rearrangement of a hydrogen atom. The striking conclusion is that the most abundant ions from these molecules are produced by rearrangement processes.

Discussion of Saturated Lactones

In discussing the spectra of the saturated lactones it is convenient to consider the β-propiolactone separately since it contains the only four-membered ring. The most intense peaks for the β-propiolactone are those which result from the rupture of two ring bonds. The high intensity at mass 42 indicates a II-IV rupture to give a $C_2H_2O^+$ fragment. The high yields of masses 26, 27 and 28 most probably arise from I-III rupture to give $C_2H_4^+$ with some subsequent dissociation. Some of the mass 28 peak may also be due to CO^+. The moderate intensities of masses 14 and 15 indicate some tendency for rupture of adjacent bonds I-II or II-III. The moderate peak at mass 29 can only be HCO^+ and probably results from dissociation of H_2CO^+ after a II-IV split. There is no indication of a parent ion at mass 72 and this is consistent with the known instability of this strained four-membered ring compound.[5]

Two of the moderately intense peaks in the spectrum of β-propiolactone are due to rearrangement. Mass 15 can only be CH_3^+ formed by rearrangement from CH_2. Similarly the mass 43 peak of 31.7 relative intensity can only be $C_2H_3O^+$ most probably from rearrangement during a II-IV split. Further consideration will be given later to these and other rearrangements.

The mass spectra of γ-butyro- and γ-valerolactone, when combined with the "isotopic" results of Table II, indicate very similar bond splitting processes in the two cases. With γ-butyrolactone the most intense peaks are at masses 28 and 42 and there are peaks of moderate intensity at masses 41, 29, 28 and 56. The large intensities at masses 28, 27 and 26 suggest that 1–3 split to give originally $C_2H_4^+$ is a very probable process. As noted earlier this is supported by the 30/28 ratios of Table II. A 1-4 split of high probability is also indicated for γ-butyrolactone since this will give $C_3H_6^+$ and explain the intense peak at mass 42 and also, by subsequent dissociation, the peaks at masses 41, 40 and 39. (The fact that CO_2, the other fragment from a 1-4 split, is not a prominent peak is simply an indication of the small tendency of CO_2^+ to form.) There is also definite evidence of a 3–5 bond split of moderate but not large probability. This split leads to the fragment $C_3H_4O^+$, and Table II shows that the 56 fragment does indeed contain the carbonyl oxygen. Finally there is no necessity to invoke either a 2–4 or a 2–5 split to explain the spectrum of γ-butyrolactone. In fact the low intensity at mass 43 argues against a 2–5 split since a $C_2H_2O^+$ ion of mass 42 from this split would be expected to give considerable rearrangement to the stable mass 43 ion whereas actually the intensity of mass 43 is rather low.

There is little evidence with γ-butyrolactone of splits of adjacent ring bonds. Thus the intensities at masses 14 and 15 are low as are those for masses around 72. The 31/29 and 30/28 ratios of Table II show that little if any of the peaks at masses 28 and 29 are due to CO^+ and HCO^+ produced by a 1–5 split and rearrangement.

The spectrum of γ-valerolactone is very similar to that of γ-butyrolactone in the mass 28 region. The most obvious differences between the two spectra, other than those in the high mass region, are that with the valerolactone the mass 56 peak is very intense, the mass 42 peak is of *low* intensity and the mass 43 peak is of moderately *high* intensity. However, these differences actually lead to the conclusion that the bond splitting processes are the same for the two lactones. The obvious explanation of the intense mass 56 peak is that it is partly due to $C_4H_8^+$ from a 1–4 bond split (the same split that accounts for the intense 42 peak with γ-butyrolactone). This is confirmed by the 58/56 ratios of Table II for the γ-valerolactone. Part of the mass 56 intensity also comes from the ion $C_3H_4O^+$ arising, as with γ-butyrolactone, from a 3–5 split. The large 28, 27 and 26 peaks for γ-valerolactone combined with the low 30/28 ratio of Table II again suggest that a 1–3 bond split is very probable. As with the γ-butyrolactone, there is little indication of a 2–4 or 2–5 bond split, nor is there indication of much split of adjacent ring bonds.

There are three moderately intense peaks in the spectrum of γ-valerolactone which are not explicitly accounted for by the above discussion, those at masses 85, 43 and 41. The mass 85 peak quite obviously comes from loss of the terminal CH_3 group and this is confirmed by the 87/85 ratios of Table II. Mass 41 probably comes from dissociation of $C_4H_8^+$ by the process

$$C_4H_8^+ = CH_3 + C_3H_5^+$$

The peak at mass 43 is probably $C_2H_3O^+$ and may arise from dissociation of $C_2H_4O^+$ following a 3–5 split.

One of the interesting problems with these saturated lactone spectra is the presence of several peaks of moderate intensity which are due to rearrangement of hydrogen atoms. Such processes are a common feature of mass spectra. For example, a recent report by Happ and Stewart[6] lists many rearrangements in the spectra of aliphatic acids and gives literature references to the various mechanisms which have been proposed to explain rearrangements. A convenient starting point for discussion of rearrangements is given in a recent paper by Rosenstock, Wallenstein, Wahrhaftig and Eyring,[7] who outline a general model for the ionization, dissociation and rearrangement processes which can occur in a mass spectrometer. The basic notion is that during the time of roughly 10^{-6} second between initial excitation of a molecule by electron impact and the start of the ion acceleration in the spectrometer the excited species can undergo many radiationless transitions among the various degrees of freedom. In the course of this redistribution of energy the ion can decompose by various paths, some of them involving rearrangements. Furthermore some of the initially formed fragments can decompose further by dissociation processes.

Such a theory does not suffice for prediction of what specific rearrangements will occur; for this one needs added assumptions. A general assumption whose utility is borne out by examination of large numbers of mass spectra is that there is a large probability of rearrangement only when one of the resulting fragments is of relatively high stability. For the specific case of mass spectra of lactones it is of interest that essentially all of the observed rearrangements lead to so-called "even electron" ions, *i.e.*, ions with even numbers of valence electrons. This is consistent with the known fact[8] that in mass spectra generally the most intense peaks are those for ions with an even number of electrons. (With spectra of compounds of normal carbon, hydrogen and oxygen these will be at odd mass numbers.) With the lactones a rupture of

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[5] (a) T. L. Gresham, J. E. Jansen and F. W. Shaver, THIS JOURNAL, **70**, 998 (1948); (b) F. A. Long and M. Purchase, *ibid.*, **72**, 3267 (1950).

[6] G. P. Happ and D. W. Stewart, *ibid.*, **74**, 4404 (1952).

[7] H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig and H. Eyring, *Proc. Nat. Acad. Sci.*, **38**, 667 (1952).

[8] (a) J. Delfosse and W. Bleakney, *Phys. Rev.*, **56**, 256 (1939); (b) catalogue of Mass Spectra Data, Carnegie Institute of Technology, Pittsburgh, Pa.

two bonds, *i.e.*, a split of the ring, leads to a "radical" ion, an ion with an odd number of electrons and one might thus expect some rearrangement.

In addition to the assumption of a stable product there are some further conditions which must be satisfied before rearrangements can occur. In the most common rearrangements observed in electron impact studies, those involving hydrogen atoms, there must be a donor C–H bond, an acceptor atom with an available orbital for bonding and an odd electron available for bonding in this orbital. The latter condition assumes that hydrogen atoms and not negative hydride ions migrate in the course of the rearrangement. It is obvious that in the major ring split for γ-butyro and γ-valerolactones, the 1–4 split in which CO_2 is eliminated and "radical" hydrogen ions are formed, a rearrangement to a more stable "even electron" ion is impossible since no donor hydrogen is available. In the prominent splits of β-propiolactone other than the I-III split the neutral fragment residue contains C–H bonds which can and do provide hydrogen atoms for the rearrangements in which the "even electron" ions, $C_2H_3O^+$ and CH_3^+, are formed. The former is frequently the most abundant product in the spectra of esters and ketones which indicates high stability and the latter is commonly observed as a rearrangement product in a variety of spectra.

Unsaturated Lactones

An inspection of the data of Table I for the three unsaturated lactones reveals some interesting variations from the results for the saturated compounds. One is the much greater intensity for all of the parent peaks of the unsaturated lactones. Another is the large intensities of "even electron" ions at masses 55, 43 and 27. A third item is the relative similarity of the patterns for the three unsaturated lactones as contrasted to the variations observed among the saturated lactones. However, it should be noted that two of the unsaturated lactones are isomeric and differ only in the position of the double bond.

The two lactones with α,β-unsaturation, γ-crotono and β-angelica, give spectra whose main features are very similar, particularly when considered from a process standpoint. As with the saturated lactones the major peaks come from a split of two of the ring bonds and splits of adjacent ring bonds are rare. The major split is that of the 3–5 bonds. Extensive rearrangement accompanies this rupture giving the large peaks at mass 55 and the data of Table II confirm the presence of the carbonyl oxygen in these mass 55 ions. The other fragments from this 3–5 split are undoubtedly responsible for most of the mass 29 peak in the crotonolactone and of the large 43 peak in β-angelicalactone. (Note that mass 43 is almost absent in the spectrum of γ-crotonolactone.) In contrast to saturated lactones, a 1–4 split is not very probable as evidenced by the low intensity of the 40 and 39 peaks of the crotonolactone and of the 54 and 53 peaks of the β-angelica. This difference may be due to some resonance stabilization of the 1 bond in the conjugated α,β-carbonyl system. Evidently 1-3 splits are moderately probable since for both lactones the peaks at masses 26 and 27 are fairly intense. There is little evidence for 2–4 or 2–5 splits for either lactone and this may be due to the strength of the 2 bond for these compounds, although it should be noted that 2–4 and 2–5 splits are not encountered even with the saturated lactones. In addition to the peaks which relate to the above discussions the β-angelicalactone gives a moderate peak at mass 83 and a smaller peak at mass 15. Both of these are undoubtedly due to rupture of the side chain bond.

In contrast to the saturated lactones with the unsaturated lactones the major peaks, other than for the parent ions, are for "even electron" ions. The major reason is that the predominant bond splits are 3–5 and 1–3, both of which permit extensive rearrangements. Thus the mass 54 fragment from a 3–5 split has an unpaired electron (or three by unpairing the π-electrons) and has also several orbitals to accept a hydrogen. Furthermore the other fragments from this split, CH_2O or C_2H_4O, have hydrogens available for donation in the rearrangement process. Finally the mass 55 ion, $C_3H_3O^+$, is probably fairly stable since it is frequently an important peak in the spectra of aldehydes and ketones. Most of the observed mass 27 peaks are probably also due to rearrangement and arguments similar to the above apply to this case.

The mass spectrum of α-angelicalactone is obviously very similar to that for the β-angelicalactone in major details. The only differences of consequence are at peaks 83, 54 and 29, none of which is a major peak in either spectrum. Although these differences are of real importance in distinguishing between the two compounds, the important problem for the present discussion is the close similarity for the two isomers of such intense peaks as those at masses 55, 43 and 27. Since the hydrolysis reactions of α-angelicalactone in aqueous solutions are complex[9] (including a strong tendency to isomerize to the β-angelicalactone) no attempt was made to introduce O^{18} into the molecule. Thus we are not sure whether the ring split which produces the peak at mass 55 is again 3–5 or whether it is 2–5. However, the ions of mass 55 and 43 which would result from a 3–5 split are both known to be of high stability and it is quite possible that the tendency to form these stable products compensates for the normally greater difficulty of breaking a C=C double bond.

The differences that are observed in the α-angelicalactone spectrum are consistent with the structure of Fig. 1f. The smaller peak at mass 29 as compared to that for β-angelicalactone is consistent with the absence of a proton on the γ-carbon. Similarly, a direct production of a $C_3H_2O^+$ ion at mass 54 is not possible with the α-angelica in contrast to the situation with the β-angelicalactone. The much smaller peak at mass 83 for the α-angelicalactone is probably a result of lower stability of the 83 fragment which in this case is not stabilized by α,β-carbonyl conjugation.

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(9) F. A. Kuehl, R. P. Linstead and B. A. Orkin, *J. Chem. Soc.*, 2213 (1950).