

A Mass Spectrometric Study of Substituted Furfuryl Compounds (1)

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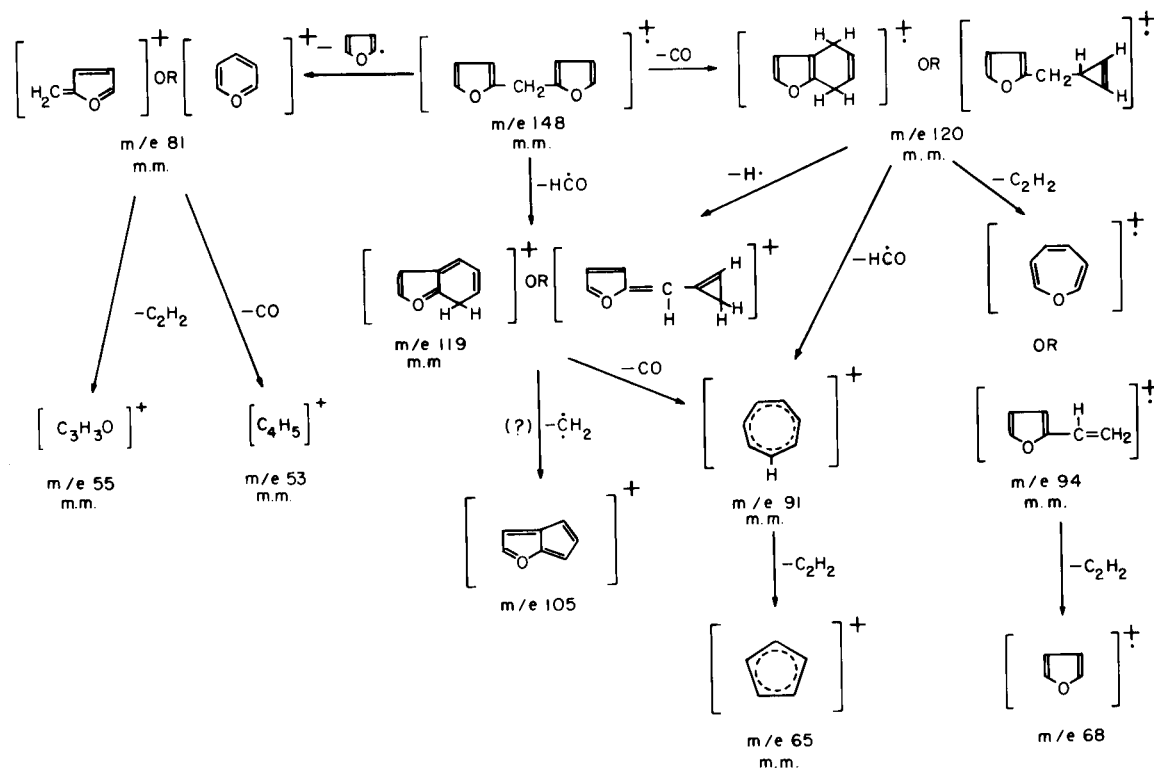
The mass spectra of six furfuryl compounds - namely, furfuryl alcohol, 5-furfuryl-furfuryl alcohol, difurfuryl ether, difurylmethane, 2,5-difurfurylfuran, and 4-furfuryl-2-pentenoic acid- γ -lactone - have been studied. Their fragmentation mechanisms are discussed in detail with particular emphasis on the modes that lead to the formation of aromatic fragments. The majority of the fragment ions are formed by elimination of CO and C_2H_2 from even-electron precursor ions and HCO from odd-electron precursor ions. Molecules containing two furan rings linked by a methylene group give mass spectra that exhibit large abundances of aromatic fragment ions.

Introduction.

Furfuryl alcohol resins are low-molecular-weight, heterogeneous polymers that are composed of many types of chemical species (3). Over the past ten years these resins have been used extensively as binders in the manufacture of graphite. Consequently, there is considerable interest

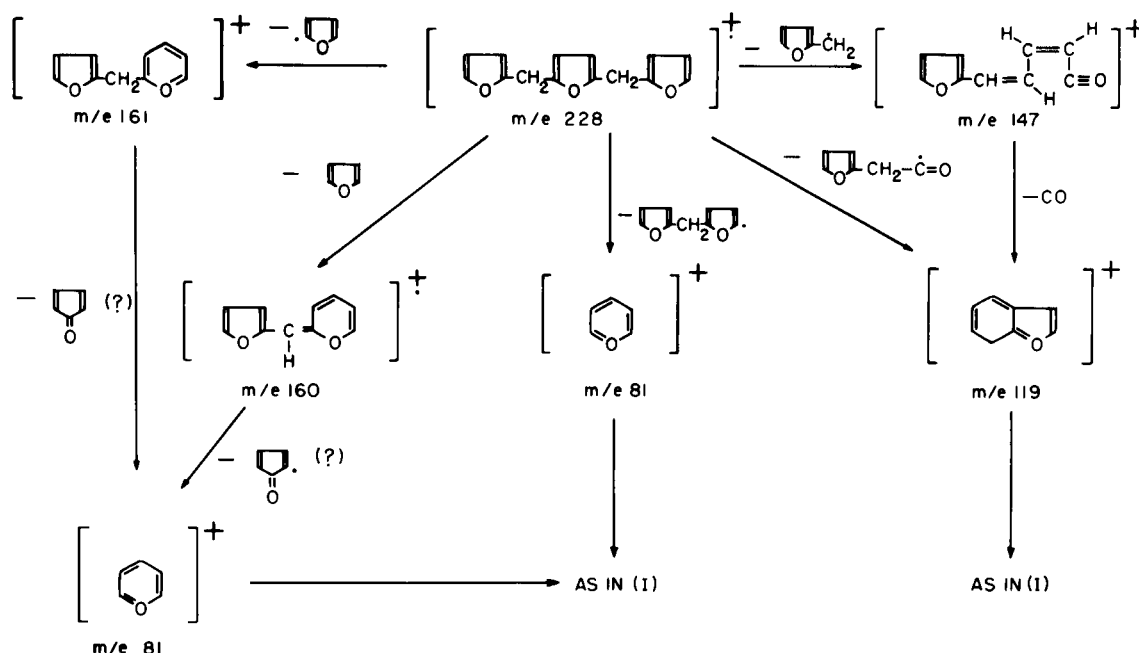
in the behavior of these resins and their component molecules during pyrolysis and carbonization. In this study, several furfuryl compounds isolated from furfuryl alcohol resins were subjected to electron-impact fragmentation, and the resultant mass spectra were obtained.

DIFURYLMETHANE (1)



Scheme I. Fragmentation pattern of difurylmethane.

2,5-DIFURFURYL-FURAN (II)



Scheme 2. Fragmentation pattern of 2,5-difurfurylfuran.

It is anticipated that it may be possible to correlate the electron-impact fragmentation behaviors of representative resin components with their conduct during thermally induced fragmentation. Although no general correspondence between electron-impact fragmentation mechanisms and pyrolytic decomposition has been observed, specific examples have been reported where a close relationship exists (4). Of particular interest to us are the mechanisms by which furfuryl compounds form benzenoid or other aromatic compounds during fragmentation or decomposition.

Recently a chromatographic technique was developed that enabled us to obtain relatively pure samples of many of the low-molecular-weight components of furfuryl alcohol resins (5). By this method, furfuryl alcohol, difurylmethane, difurfuryl ether, 5-furfuryl-furfuryl alcohol, 2,5-difurfurylfuran, and 4-furfuryl-2-pentenoic acid- γ -lactone were collected and their mass spectra investigated. Also discussed herein are proposed mechanisms, which account for the formation of the major fragment ions observed in the mass spectra of each compound.

Discussion.

Compounds containing furfuryl groups are somewhat difficult to obtain by synthetic means, and consequently little detailed mass-spectral information concerning these compounds is available. Generally, the mass spectra of the

six components studied by us tend to resemble those of simple furan molecules as reported by other authors (6-10); that is, the formation of the more abundant fragment ions involves the loss from precursor ions of simple neutral molecules or radicals. Such species as CO, HCO, and C_2H_2 , which are often observed to be mass-spectral fragmentation products, are likely to be products of pyrolytic

TABLE I

Metastable Transitions

| Compound | m_1 | m_2 | Neutral | m^* |
|---------------------|-------|-------|-------------------------------|----------|
| Difurylmethane | 120 | 119 | 1 (H) | 118.0 |
| | 148 | 120 | 28 (CO) | 97.3 |
| | 147 | 119 | 28 (CO) | 96.3 (a) |
| | 148 | 119 | 29 (HCO) | 95.7 |
| | 119 | 91 | 28 (CO) | 69.6 (b) |
| | 120 | 91 | 29 (HCO) | 69.0 |
| | 94 | 68 | 26 (C_2H_2) | 49.2 |
| | 91 | 65 | 26 (C_2H_2) | 46.4 (c) |
| 2,5-Difurfurylfuran | 199 | 171 | 28 (CO) | 147.0 |
| | 228 | 147 | 81 (furfuryl) | 95.0 |

(a), (b), and (c) present in this spectrum also.

decomposition also. Thus, delineation of fragmentation mechanisms involving elimination of these moieties might furnish some insight into the processes by which various carbonaceous structures are formed during the pyrolysis of furfuryl alcohol resins.

In the following sections, the 70-ev mass spectra of the selected furfuryl compounds are discussed with particular emphasis given to their common fragmentation characteristics. Postulated mechanisms are set forth for the formation of the more prominent ions in each spectrum, although in several cases low-abundance fragments are discussed because of their importance in characterizing the given compound.

There are several instances in the proposed mechanisms where a particular fragment ion could be formed through a concerted rather than a stepwise fragmentation path. However, except for one or two instances only stepwise fragmentation schemes are described. In all cases where a cyclic structure appears reasonable, such an ion is proposed, although in some instances equally probable alternative structures are displayed.

There are several places in the postulated mechanisms where a choice can be made between the formation of small or large ring structures. We prefer to write mechan-

isms that involve larger ring structures (particularly where five- to eight-member rings can be drawn) primarily because of their greater stability. Without more detailed information, such as that derived from the mass spectra of labeled derivatives, it is often difficult to choose unequivocally between the various structural possibilities. Other authors, e.g. Collin (12) and Cooks (13), have discussed the formation of both cyclic ions and cyclic neutral fragments in mass-spectral investigations of substituted furans and other types of unsaturated compounds.

The mass spectra are presented as bar graphs with the ordinate labeled "Relative Abundance"; the most intense peak (base peak) is set equal to 100%. Also included on the graphs are the nominal masses of the more abundant peaks in each spectrum. The letters "m.m.", which appear in the fragmentation mechanism illustrations, indicate that the empirical formula of the designated ion was established by precise mass measurement.

(a) Difurylmethane (I) and 2,5-Difurfurylfuran (II).

The mass spectrum of I has been discussed briefly by Biemann (6) and was mentioned by Stoll *et al.*, (11) although no detailed discussion of possible fragmentation modes was given by either of these authors. Figure 1 (a)

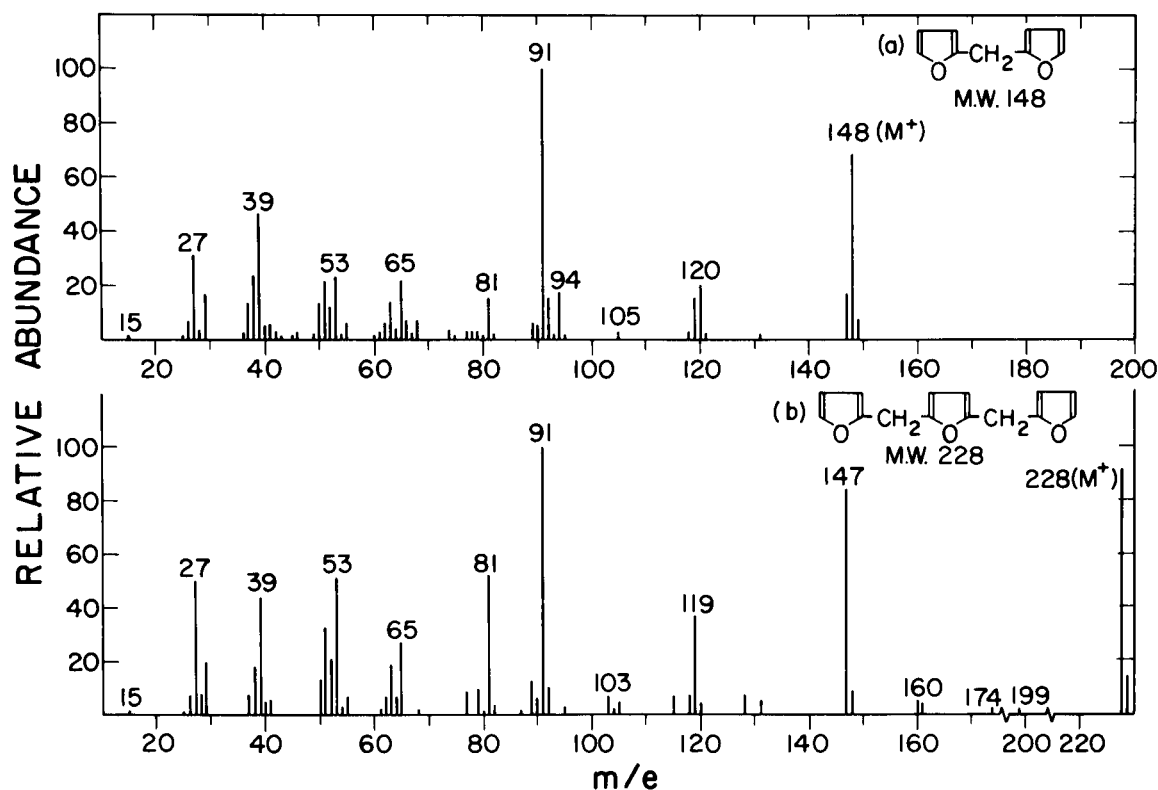
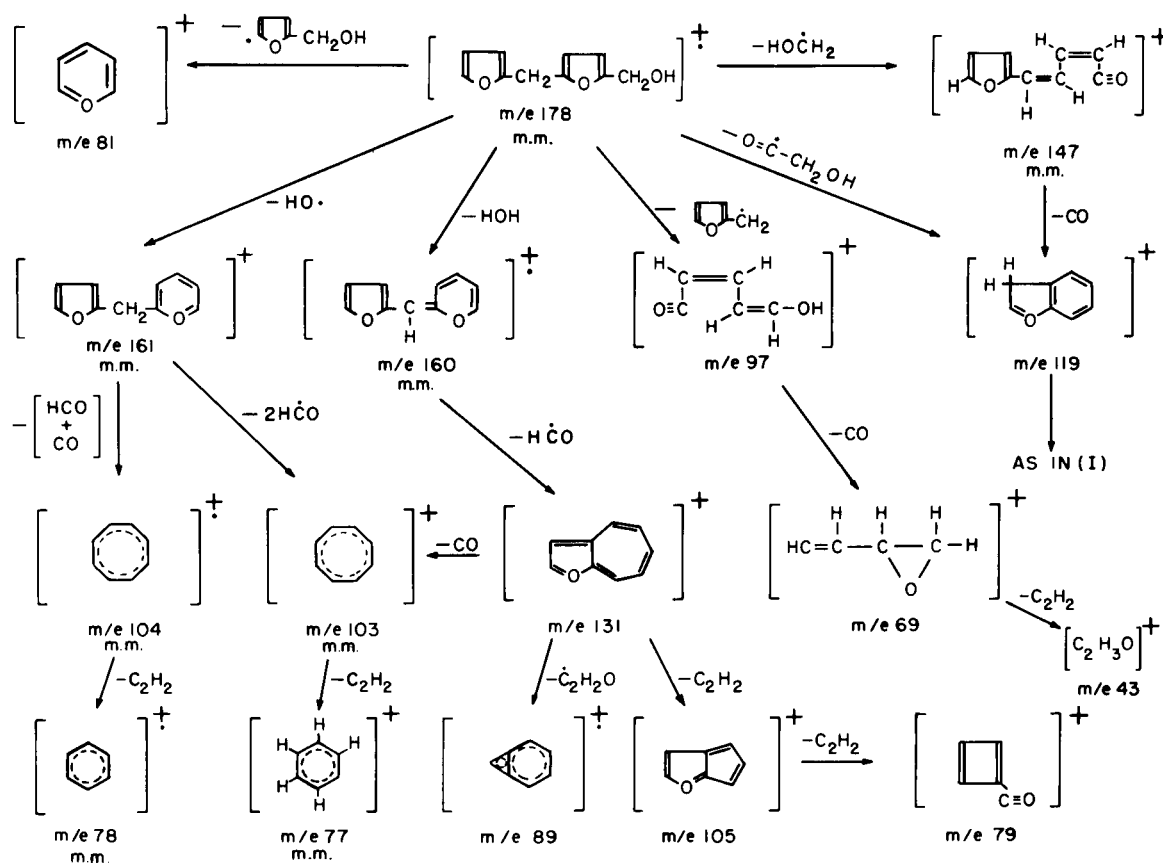


Figure 1. Mass spectrum of difurylmethane (a) and 2,5-difurfurylfuran (b).

5-FURFURYL-FURFURYL ALCOHOL (III)



Scheme 3. Fragmentation pattern of 5-furfuryl-furfuryl alcohol.

displays the spectrum of I obtained in this study, and Scheme 1 illustrates the fragmentation mechanisms that we postulate to account for the occurrence of the more prominent peaks in its mass spectrum. The spectrum of II is shown in Figure 1 (b), and the proposed fragmentation modes for this compound appear in Scheme 2.

Of particular interest in these spectra is the abundance of the m/e 91 ion, which is the base peak (100%) in both spectra. Precise mass measurements identified this ion as $[\text{C}_7\text{H}_7]^+$; it is presumably the tropylium ion. The $[\text{C}_7\text{H}_7]^+$ ion is formed by the elimination of small fragments from the parent ion of I, but more complicated fragmentations are proposed to account for the formation of tropylium ion in the case of the higher homolog (II). These postulated fragmentations are supported by metastable-ion peaks present in both spectra, as detailed in Table I. Subsequent fragmentation of the $[\text{C}_7\text{H}_7]^+$ ion accounts for the major portions of both spectra below m/e 67, including the relatively large m/e 65 peak.

As one would expect, the spectra of both compounds are quite similar below m/e 148 except for two noteworthy exceptions. The m/e 81 peak in the spectrum of I is relatively small compared to the approximately 50% abundance of the corresponding peak in the spectrum of II; precise mass measurements in both cases identify this ion as $[\text{C}_5\text{H}_5\text{O}]^+$. The higher resonance stability of the 5-furfuryl-2-furyl radical relative to that of the furyl radical, as well as a statistical advantage, quite likely accounts for most of the enhancement of the m/e 81 ion in the spectrum of II. The other exception is the presence of the m/e 120 ion in the mass spectrum of I, which results from the loss of 28 mass units (CO) from the parent ion. The corresponding ion, m/e 200, is missing in the spectrum of II. Apparently the facile fragmentation of the molecular ion of II into odd-mass fragment ions (e.g., m/e 147 and m/e 119) precludes the formation of any appreciable amount of the type of ion proposed for m/e 120 (Scheme 1). It is interesting to note that the majority of fragment

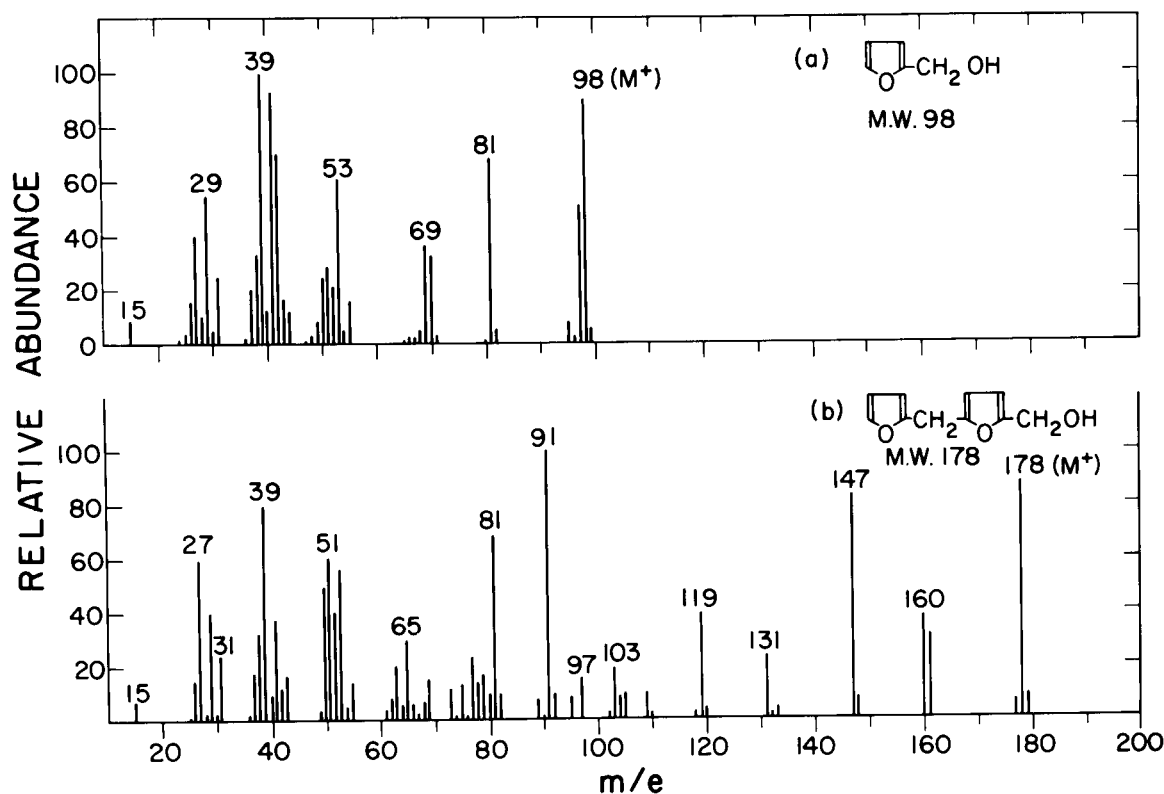


Figure 2. Mass spectrum of furfuryl alcohol (a) and 5-furfuryl-furfuryl alcohol (b).

ions (in terms of relative abundance) in both spectra are even-electron ions resulting from the loss of HCO from an odd-electron precursor or the loss of CO and/or C₂H₂ from even-electron precursors.

The low-voltage (~15 eV ionizing voltage) mass-spectral patterns of these two compounds reveal an enhancement of the parent ion [M]⁺, of the [M-CO]⁺ fragment ion (m/e 120) in the case of I, and of the [M-81]⁺ fragment (m/e 147) in the spectrum of II, with a consequent decrease in the [C₇H₇]⁺ (m/e 91) ion in both spectra. Of interest also is the fact that the [C₆H₆O]⁺ (m/e 94) ion in the spectrum of I increases slightly in intensity relative to m/e 91, lending support to the proposal that the m/e 120 ion is the precursor of the m/e 94 ion.

(b) 5-Furfuryl-Furfuryl Alcohol (III).

Figure 2(a) displays the spectrum of furfuryl alcohol obtained in this study and Figure 2(b) that of III. The mass spectrum of the former compound has been discussed in detail by Collin (12). The outstanding difference between the two spectra is the large m/e 91 (100%) fragment ion in the spectrum of III. (An m/e 91 fragment is not possible in the case of furfuryl alcohol). Scheme 3 details the proposed fragmentation mechanisms responsible for the formation of the m/e 91 ion as well as

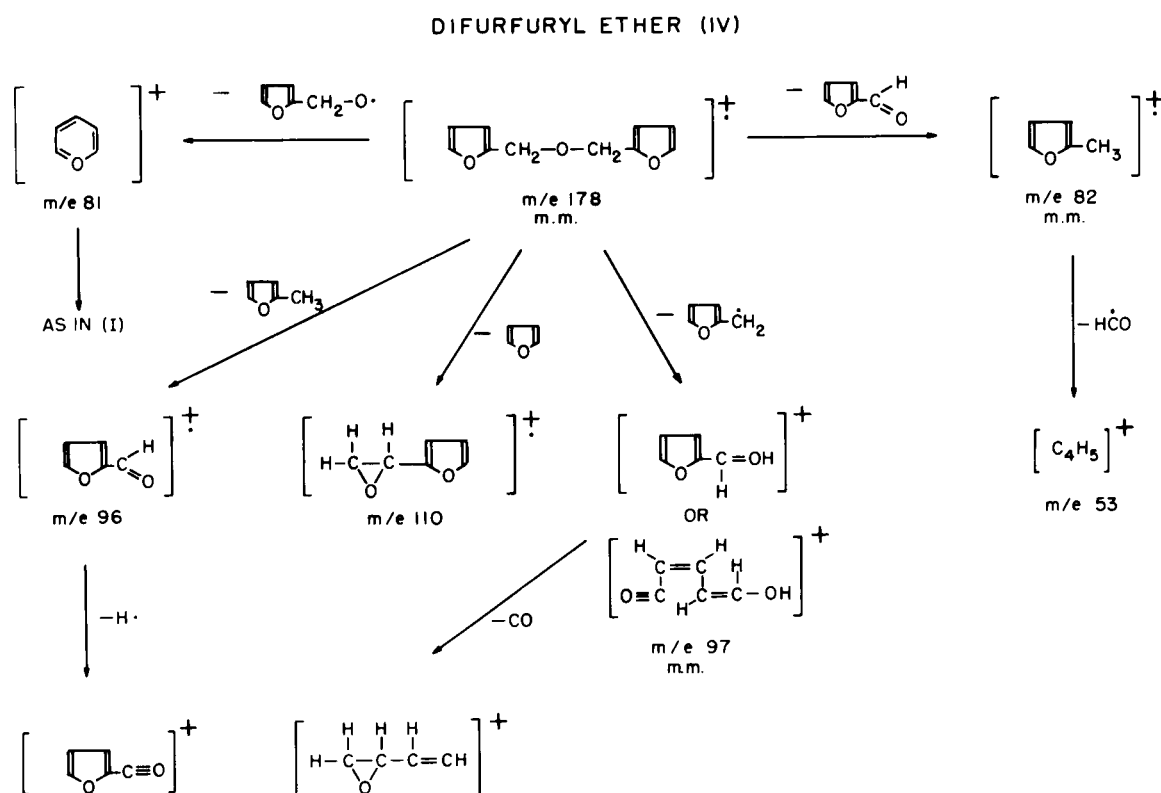
a number of the other abundant fragment ions in the spectrum of III. It might be expected, because of structural similarities, that the latter stages of the fragmentation of III would be similar to those of II. Indeed, a comparison of the spectra in Figures 1(b) and 2(b) reveals similarities especially below m/e 160, and particularly with regard to the more abundant fragment ions.

The most distinguishing features of the spectrum of III (compared to the other furfuryl derivatives) are the peaks at m/e 161 [M-OH]⁺, m/e 160 [M-H₂O]⁺, and m/e 31 [CH₂OH]⁺. As can be seen in Scheme 3, cyclic structures have been proposed for many of the fragment ions of III, including an eight-membered ring for m/e 103 and 104 (14). As mentioned earlier, such structures, for the most part, have been postulated on the assumption that they

TABLE II

Metastable Transitions

| Compound | m ₁ | m ₂ | Neutral | m* |
|-----------------------------|----------------|----------------|-------------------------|-------|
| 5-Furfuryl-Furfuryl Alcohol | 178 | 161 | 17 (OH) | 145.6 |
| | 178 | 160 | 18 (HOH) | 143.8 |
| | 178 | 147 | 31 (CH ₂ OH) | 121.4 |



Scheme 4. Fragmentation pattern of difurfuryl ether.

represent the more stable form of the ion (13) and, in addition, are more suitable precursor structures for further plausible fragmentation routes. For the sake of simplicity, we show (in Scheme 3) the m/e 103 and 104 ions as forming directly from the m/e 161 ion through the simultaneous loss of two neutral moieties, although it is more likely that stepwise loss occurs as in the m/e 160- m/e 131- m/e 103 sequence.

Table II lists the prominent metastable peaks observed in the mass spectrum of III, which have resulted from the fragmentation of the alcohol functional group.

(c) Difurfuryl Ether (IV).

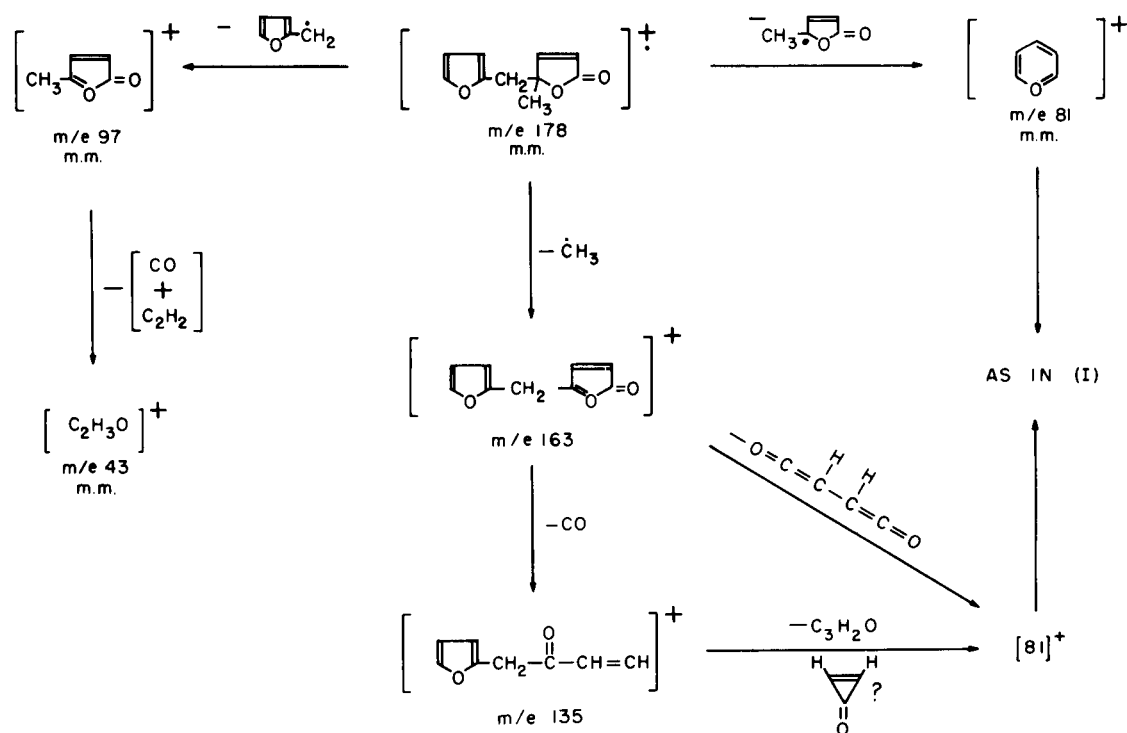
Only brief reference has been previously made to the major peaks in the mass spectrum of IV, this in an article by Stoll *et al.* (11). We found the mass spectrum of IV to be relatively simple, with about 30% of the total ion current carried by the m/e 81 ion. [See Figure 3(a) for the mass spectrum obtained in this study]. The parent ion accounts for less than 2% of the total ion current.

Scheme 4 illustrates the fragmentation mechanisms proposed to account for the most prominent peaks in the mass spectrum of IV. Because of the presence of the aromatic, heterocyclic ring attached to both of the carbon atoms adjacent to the ether O atom, ions resulting from

fragmentation of the bonds β to this O atom (a mechanism evident in the mass spectra of aliphatic ethers (7)) are minor contributors to the mass-spectral pattern of this ether. However, a small peak at m/e 110 is observed that presumably results from cleavage of the β -carbon bond in the molecular ion. This, together with proton transfer, results in a furan molecule, and probably a furyl-substituted ethylene oxide ion (m/e 110). IV is unique among the compounds investigated in this study in forming the m/e 110 ion, and the appearance of this ion aids in the identification of IV. The ease with which the ether C-O bonds cleave apparently reduces the relative importance of the mechanisms involving loss of HCO and CO from the molecular ion.

An interesting mechanism is that which produces the abundant m/e 82 ion. Cleavage of either bond α to the ether O atom, together with a hydrogen atom transfer from the opposite methylenic group, results in the formation of two stable species, methyl furan and furfuraldehyde. The positive charge prefers to reside with methyl furan (the ratio of m/e 82 to 96 is about 15/1). The sizeable m/e 53 ion is the result of a relatively abundant methyl furan precursor; the ion is not nearly as pronounced in the spectra of the other compounds. Table III lists many of the metastable transitions observed in the spectrum of

4-FURFURYL-2-PENTENOIC ACID-
 γ -LACTONE (V)



Scheme 5. Fragmentation pattern of 4-furfuryl-2-pentenoic acid- γ -lactone.

IV, most of which are associated with the decomposition of the m/e 81 and 82 ions.

The absence of a sizable m/e 91 peak in the spectrum of IV is noteworthy. Only the most complicated, and consequently less favorable, fragmentation mechanisms can be postulated for the formation of a $[C_7H_7]^+$ in this case. In fact, very few non-heteroaromatic ions are observed in the mass spectrum of IV.

(d) 4-Furfuryl-2-Pentenoic Acid- γ -Lactone (V).

It is apparent, upon examination of the mass spectrum displayed in Figure 3(b), that there are several peaks that distinguish this furfuryl compound. The m/e 163 ion, $[M-CH_3]^+$, and the m/e 135 ion, $[M-CH_3-CO]^+$, set this spectrum apart from the others described above. Also, the intensity of the m/e 43 ion, $[C_2H_3O]^+$, is enhanced in the spectrum of this compound. Otherwise its spectral pattern is similar to those of several of the other furfuryl derivatives. The most abundant ion is m/e 81 (35% of the total ion current), as compared to a parent-ion abundance of about 1.5% of the total ion current. Although slightly larger than in the case of IV, the m/e 91 ion is small, accounting for less than 2% of the total ion current.

Scheme 5 shows the fragmentation mechanisms proposed for the formation of the more important ions in

the mass spectrum of V. The observed metastable-ion spectrum is quite similar to that of IV, with the most pronounced peaks being associated with decomposition of the m/e 97 and 81 ions. (See Table III).

In summary, the mass spectra of substituted furfuryl compounds that contain two furan rings linked by a methylene group exhibit large abundances of aromatic fragment ions. The formation of these ions can often be explained by the stepwise loss of simple neutral species such as CO, HCO, and C_2H_2 from the parent ion. From

TABLE III

Metastable Transitions

| Compound | m_1 | m_2 | Neutral | m^* |
|------------------|-------|-------|-----------------|----------|
| Difurfuryl Ether | 82 | 81 | 1 (H) | 80.0 (a) |
| | 97 | 69 | 28 (CO) | 49.1 (a) |
| | 81 | 55 | 26 (C_2H_2) | 37.3 (a) |
| | 82 | 54 | 28 (CO) | 35.6 |
| | 81 | 53 | 28 (CO) | 34.7 (a) |
| | 82 | 53 | 29 (HCO) | 34.2 |

(a) Also observed in spectrum of lactone derivative.

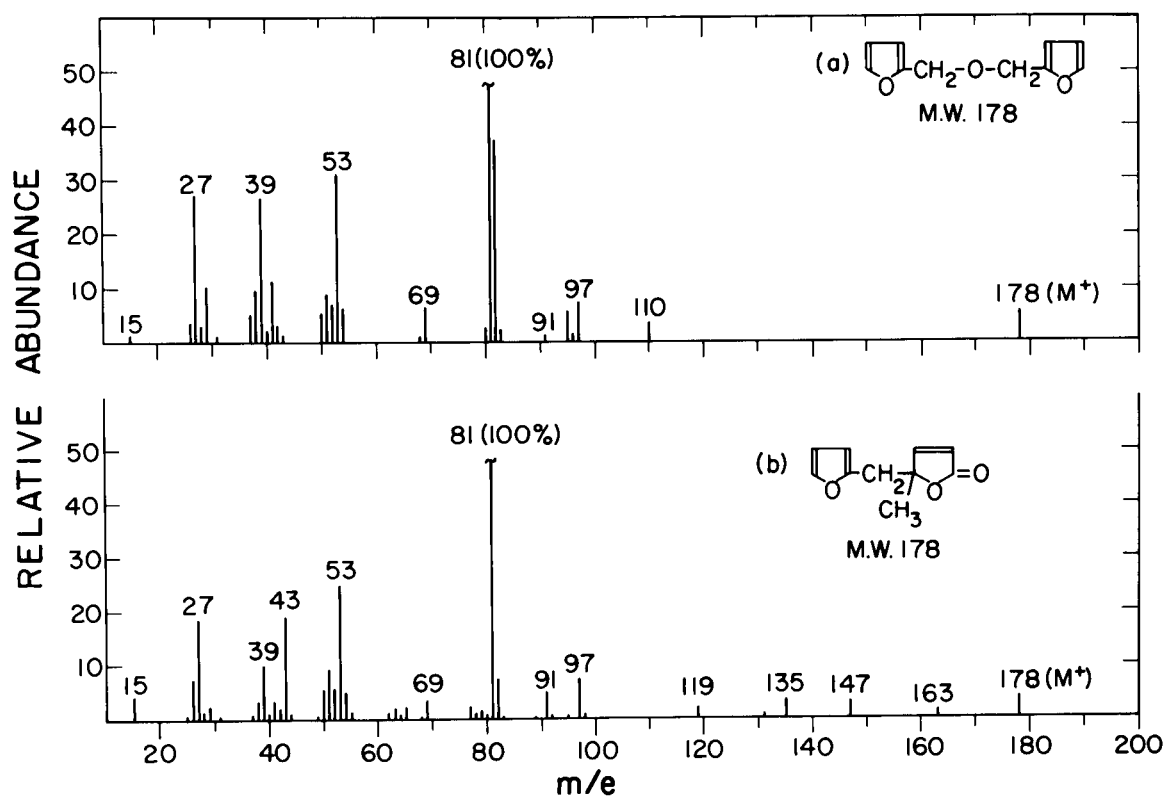


Figure 3. Mass spectrum of difurfuryl ether (a) and 4-furfuryl-2-pentenoic acid- γ -lactone (b).

the examples reported here, it should be possible to predict the character of the mass spectra of many other furfuryl compounds. The mass-spectral information leads to the suggestion that those compounds that produce mass spectra containing large amounts of aromatic ions might also result in more highly graphitic carbon structures upon pyrolysis. A study of such possible correlations will be the object of experiments to be initiated in the near future.

EXPERIMENTAL

The furfuryl compounds studied in this work were isolated from either a maleic anhydride-polymerized or a γ -alumina-polymerized furfuryl alcohol resin, both of which had viscosities of about 250 cp. The latter resin was the source of 4-furfuryl-2-pentenoic acid- γ -lactone; the other components were isolated from the maleic anhydride-polymerized resin.

The maleic anhydride-polymerized resin was made by methods previously reported (5) and the γ -alumina-polymerized resin was made by the method of Nielsen (17). The furfuryl compounds were separated from the resins by a gas-chromatographic technique detailed elsewhere (5). The identities and purities of the separated resin components were established by ir, nmr, and ms analyses as outlined previously (5).

The 70-ev, low-resolution mass spectra were obtained with a CEC 21-103C mass spectrometer. All samples were introduced as liquids into a stainless-steel inlet system maintained at 100°; a silicone rubber dam-hypodermic syringe technique was used. The

ion source chamber was operated at 250°. Precise mass measurements on several ions were obtained on a CEC-21-110B mass spectrometer equipped with an electronic peak-matching accessory. The precision of measurement was sufficient (± 0.005 amu) to arrive unambiguously at the empirical formulae for the ions.

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bombarding energies, an eight-membered ring structure satisfactorily explained their mass-spectral data. However, at an electron energy of 70 eV, and particularly considering the ions formed in the ion-source region of their double-focusing mass spectrometer, they concluded that a styrene structure best represented their fragmentation data. We chose to represent the m/e 103 and 104 ions in the spectrum of 5-furfuryl-furfuryl alcohol as eight-membered ring structures (cyclooctatetraenes) as they form plausible precursors for the m/e 77 and 78 ions, although an *o*-xylidene-type structure as discussed by Bieman (6) and Lumpkin (16) is a reasonable alternative.

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