Chemistry of Thienopyridines. XXI. Mass Spectra of Some
Parent Compounds and Their Hydroperchlorate Salts (1)

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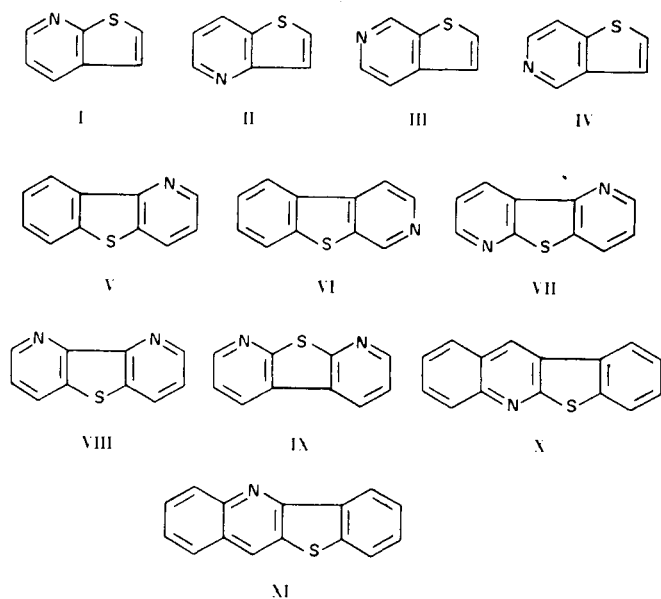Department of Chemistry, University of Oregon, Eugene, Oregon 97403

Mass spectral fragmentation patterns are reported for ten parent thienopyridines containing 2-4 rings. Several spectra were determined directly on crystalline hydroperchlorate salts, which produced pure spectra of the azine components (devoid of all peaks for perchloric acid or its decomposition products). Consistent with aromaticity in the thienopyridines are formations of both singly (most abundant) and doubly charged molecular ions, as well as (M-1) ions. Losses of hydrogen cyanide and carbon monosulfide (or thioformyl radical) occur from the molecular ions.

As part of our effort to elaborate the chemical characteristics of thienopyridines we investigated the mass spectral fragmentation patterns of a series of bicyclic (I-III), tricyclic (V-IX), and tetracyclic (X,XI) compounds at 70 eV. A novel experimental approach which we used was the direct

introduction of crystalline hydroperchlorate salts of four of the thienopyridines (I-III,IX) into the ion source of the mass spectrometer.

In previous research (3) we found that crystalline hydroperchlorate salts of quinoline and various thienopyridines are easily prepared in water or aqueous ethanolic solvents

and are readily recrystallizable therefrom. In contrast to many amine hydrochlorides and hydrobromides our hydroperchlorates are not hygroscopic. They appear to be stable to storage and melt sharply without decomposition. While it is difficult to store II as the free base, II can be kept either as the hydroperchlorate or the picrate at room conditions indefinitely.

In earlier investigations unstable or purified amines have been introduced into the mass spectrometer as hydrochlorides, hydrobromides (4a, 5-7), or picrates (7,8). However, the spectrum of the free acid (from dissociation of the amine salt) is superimposed on that of the free amine. The appropriate spectrum of the amine is then obtained by difference. Since the mass spectrum of anhydrous perchloric acid consists of a variety of chlorine-bearing ions (9), one might anticipate that azinium perchlorates would yield analogous superimposed spectra of the basic and acidic components. However, our perchlorate samples showed *no mass spectral evidence for the presence of perchloric acid*, oxidation products, or chlorine-bearing fragments.

As a check on the use of azine hydroperchlorate salts for obtaining accurate mass spectra of the azines *per se*, we compared (a) the spectrum obtained from quinolinium perchlorate with that reported for quinoline (10), (b) the spectra of I and its hydroperchlorate, and (c) the spectrum of III hydroperchlorate with that recorded for III (11). In the first two cases the corresponding spectra were quantitatively reproduced throughout. *i.e.*, for m/e values greater than 34 the relative abundances of corresponding ions agreed within ±2% (absolute value). For case (c) only two peaks differed in intensities by more than 2% (12). It is

thus apparent that the azinium perchlorates undergo facile dissociation in the heated ion chamber of the mass spectrometer and that the perchloric acid formed completely escapes detection. In fact, experimentally it was much easier to handle the hydroperchlorates in the mass spectrometer than to handle the amines themselves. Source temperatures of 110-170° were used for these salts (13).

While no examples of the use of azine hydroperchlorates in mass spectra were found in the literature, the mass spectra of some quaternary azinium perchlorates have been reported. Kramer et al. (14) found that thermal decomposition (at ca. 280°) of the pyridothiazolopyridazinium perchlorates XII and XIII (MClO₄) precedes ionization to produce abundant pseudomolecular ions at (M-1)⁺. In the

XII   XIII

a: R = C₆H₅
b: R = CH₃

two complete spectra which are presented in the paper there are no peaks which can clearly be ascribed to perchloric acid or its fragmentation products. Salsmans and van Binst (15), on the other hand, found that the mass spectra of a number of N-methylazinium perchlorates (MCH₃ClO₄) consist primarily of superimposed spectra for methyl perchlorate and the free base M. However, significant peaks also occurred at (MCH₂O)⁺ due to internal redox reactions, and chlorination products were sometimes apparent. Internal redox has also been noted in the mass spectra of 2,4,6-triphenylpyrylium and 2,4,6-triphenylthiopyrylium perchlorates (16).

The most abundant ion present in the mass spectrum of each thienopyridine (or its hydroperchlorate) is the molecular one. Significant, common fragmentation patterns for these compounds are presented in Table I. Consistent with aromaticity in the thienopyridines are the formation of appreciable peaks for (M-1)⁺ and M⁺⁺ ions in every case (4c, 17). In two cases (VI and X) there are also fragments (7%) for (M-2)⁺ ions, possibly of aryne structure (17). Evidence for the presence of a pyridine ring in the molecule is provided by the ejection of hydrogen cyanide from the molecular ion (18a). Likewise loss of either carbon monosulfide or thioformyl radical (or both) characterizes the presence of a thiophene ring (18b). In fact, compounds VI and VIII have fragments (9-13%) which correspond to loss of both (HCN + CS) and (HCN + ·CHS) from the molecular ion.

Compounds VI and VIII are particularly prone to fragmentation in a variety of ways. The (M+1)⁺ peaks are much larger than correspond to natural isotopic abun-

[Table I omitted — rotated]

dances. They must be ascribed to intermolecular trans-
ference of hydrogen on electron impact. In fact, the
appreciable intensities for both $(M+1)^+$ and $(M-1)^+$ peaks
in the spectra of these two compounds are consistent with
such an intermolecular process. Compound VIII is the
only one which loses acetylene readily and which has a
high intensity for the ion at mass number 39.

The four bicyclic compounds I-IV show closely similar
spectra (11) with intensities of $\leq 10\%$ for all (or nearly all)
of the fragment ions formed. Likewise, spectra of the two
tetracyclic compounds X and XI are very nearly identical
and show only low-intensity fragmentation ions.

EXPERIMENTAL

Purified hydroperchlorate salts of quinoline, I-III and IX were
available from previous research (3), as were the free thienopyri-
dines I, V-VIII, X and XI (19-21). Mass spectra of these samples
were determined by direct introduction of crystalline (or neat
liquid in the case of I) samples into the ion source of a CEC model
21-110 double-focusing mass spectrometer, operated at 70 eV.

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(12) One of these descrepancies was in the $(M+1)^+$ peak, reported
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isotopic abundances 8.8% (4b). The other was in the mass 44 peak:
none reported; found 9%.

(13) At this point we have not investigated the mass spectra of
any aliphatic amine hydroperchlorates. However, the potential
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