

Mass Spectra Splitting of some Compounds Containing Both Azulenic and Thiophene Moieties

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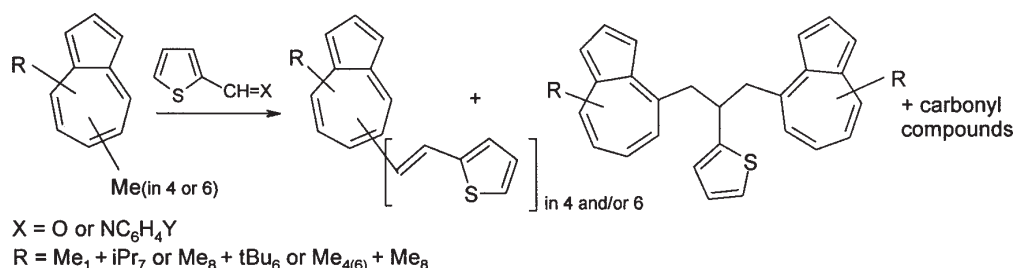
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The splitting in the electrospray ionization mass spectrometer of several azulenes substituted in seven-membered ring with 2-thien-2-ylvinyl moiety was analyzed and some general features of fragmentation were evidenced. The fragmentation of propane substituted with azulenes and thienyl moieties was also discussed. Both classes of compounds are obtained in the condensation of alkylazulenes with thiophenealdehyde or the corresponding azomethyne.

Keywords: mass spectroscopy, mass fragmentations, azulene, thiophene

As the molecular weight has been determined by the mass spectrometry, available UV, NMR or IR spectra and some chemical knowledge must be used to determine the molecular structure. Also the fragmentations occurring in mass spectrometer frequently offer valuable information about the molecular structure. Interpretation of the obtained results is often complicated by the fact that the reactions that take place in the mass spectrometer are different from these occurring in the "normal" reaction conditions. The modern technique used recently in this field e. g. electrospray ionization method (ESI), allows however

methanol to the 1 mmol/L and direct infused into the interface by a Prostar 240 chromatographic pump and the flow was set to 20 $\mu\text{L}/\text{min}$. Air was used as drying gas at a pressure of 18 psi and 150°C. The nebulising gas was nitrogen to 40 psi and the capillary voltage had been established to the potential +5000 V for positive ionization. Thus protonated molecular ion obtained was selected by the first quadrupole. Into the second quadrupole the protonated molecular ion was fragmented by collision with an inert gas (argon) to 1 mtorr pressure. Fragments were analyzed by the third quadrupole. By plotting abundance of



Scheme 1

more precise structures assignment. Our early interest on the 2-aryl-1-(azulene-1-yl)ethenes¹ already covered some considerations on their mass spectra [2]. One of the compound synthesized by us in this series was 2-[(E)-2-azulen-1-ylvinyl]thiophene. Later we have extended our study on other thienylvinyl-azulenes.³ As shown in Scheme 1, we have obtained these compounds in the condensation of alkylazulenes with thiophenealdehyde or with the corresponding azomethynes. Together with the substituted ethenes and propanes some ketones and "oligomers" are formed.

We have considered the opportunity to examine in this paper only the fragmentation of unsaturated and saturated hydrocarbons substituted by azulene-1-yls and thien-2-yl moieties. For our research we have used ESI mass spectrometer and the results are compared with these for the 1-thiethylvinyl substituted azulene, already reported.

Experimental part

The used device and fragmentation conditions

Varian 1200 L/MS/MS triple quadrupole mass spectrometer fitted with an electrospray (ESI) ionization interface was used. The substances were dissolved in

fragments versus collision energy between 0-50 eV will give breakdown curves. Prior to these experiments it was performed the tuning of mass spectrometer using PPG both for positive and negative.

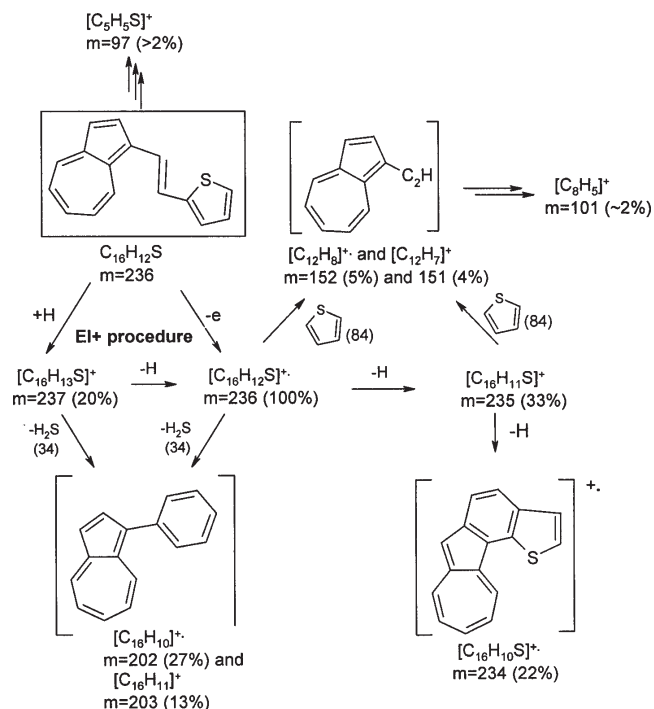
Results and discussions

The obtained mass spectrum for the 2-[(E)-2-azulen-1-ylvinyl]thiophene was obtained using EI+ procedure and the molecular weight was registered as radical-cation as well as protonated species (scheme 2).

Despite the difference from the ESI procedure some bond splittings remain common. Thus the lost of hydrogen sulfide or of the stable thiophene molecule will be encountered also for the thienyl substituted compounds studied in this paper. It is interesting to note the presence in the MS of the cations C_5H_5^+ and C_8H_5^+ common for both compound classes. At the same time, the generation of the radical-cation as $\text{C}_{16}\text{H}_{10}^+$, with $m = 234$, is specific only for the compounds with azulene substituted in position 1.

Regarding the mass spectra of the analyzed compounds two types of bond splitting can be distinguish, the

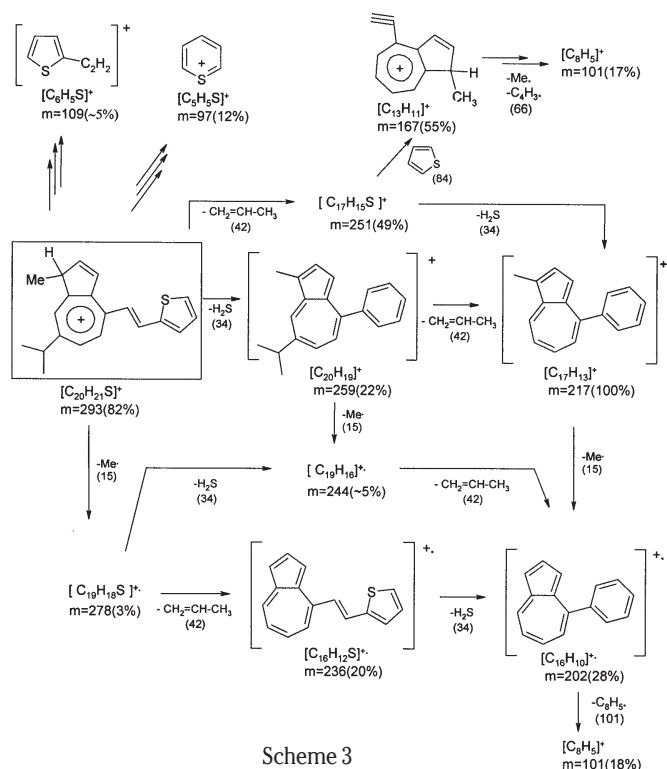
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Scheme 2

fragmentations of the alkyl substituted on azulene and the fragmentation that implies the thienylvinyl moiety. The most of these fragmentations are common for the analyzed compound. Therefore, the fragmentations of the first compound will be discussed in detail and for the other compounds only some peculiarity will be signaled.

As it is well known, in the ESI procedure the molecular ion appear as a protonated species. The protonation of 2-[(*E*)-2-(7-isopropyl-1-methylazulen-4-yl)vinyl]thiophene could occur at sulphur atom or mainly at the 1-position in azulene as is represented in scheme 3. The loss of methyl radical from the generated cation is followed by the elimination of 2-propyl group as propene. These eliminations are also encountered from the fragments generated on other ways. The loss of sulphur containing moiety occurs on several routes. The elimination of H_2S is favored by the stable phenyl ring generation. Thiophene splitting is the other route continued by the elimination of $Me\cdot$ and $C_4H_3\cdot$ radicals. For the compounds containing thienylvinyl group the cation $C_6H_5S^+$ is common.

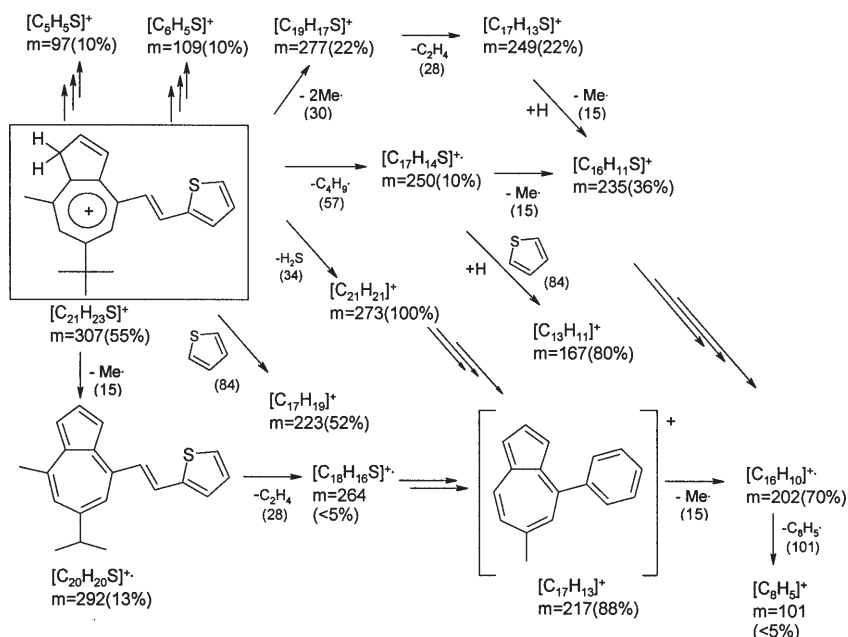


Scheme 3

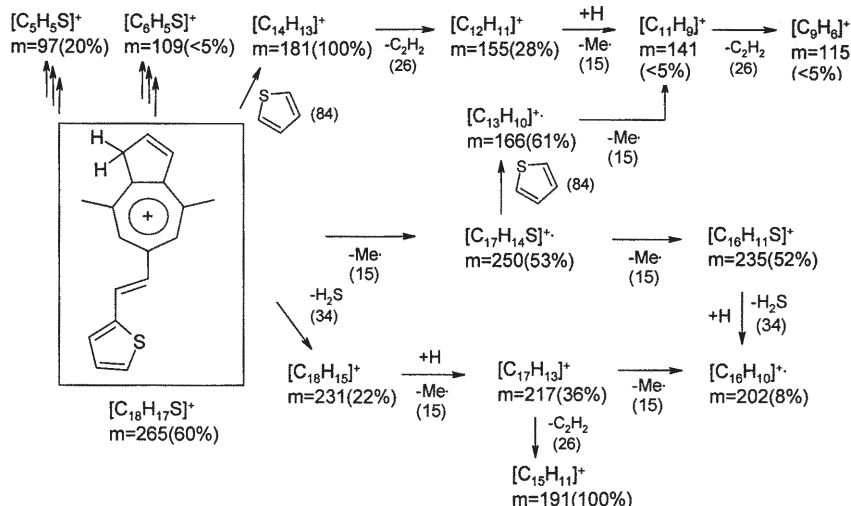
It is interesting to observe that in mass spectra of all studied compounds as well as for the 1-substituted azulene with thienylvinyl the stable aromatic cation $C_5H_5S^+$ is present.

The inspection of 2-[(*E*)-2-(8-methyl-6-*tert*-butylazulen-4-yl)vinyl]thiophene mass spectrum, represented in scheme 4, shows the specific fragmentation of *tert*-butyl group, namely $Me\cdot$ and ethane elimination however also the radical $C_4H_9\cdot$ seems to be split from the original cation. The proposed routes in the scheme 4 are in accordance with the other fragments that are present in mass spectrum. It must be however signaled the hydrogen atom transfer for several reaction routes.

As it can be seen from scheme 5, the fragmentations of protonated 2-[(*E*)-2-(4,8-dimethylazulen-6-yl)vinyl]thiophene respect most of the above discussed routes. As a novelty, along to the hydrogen atom transfer, here the acetylene lost is observed.



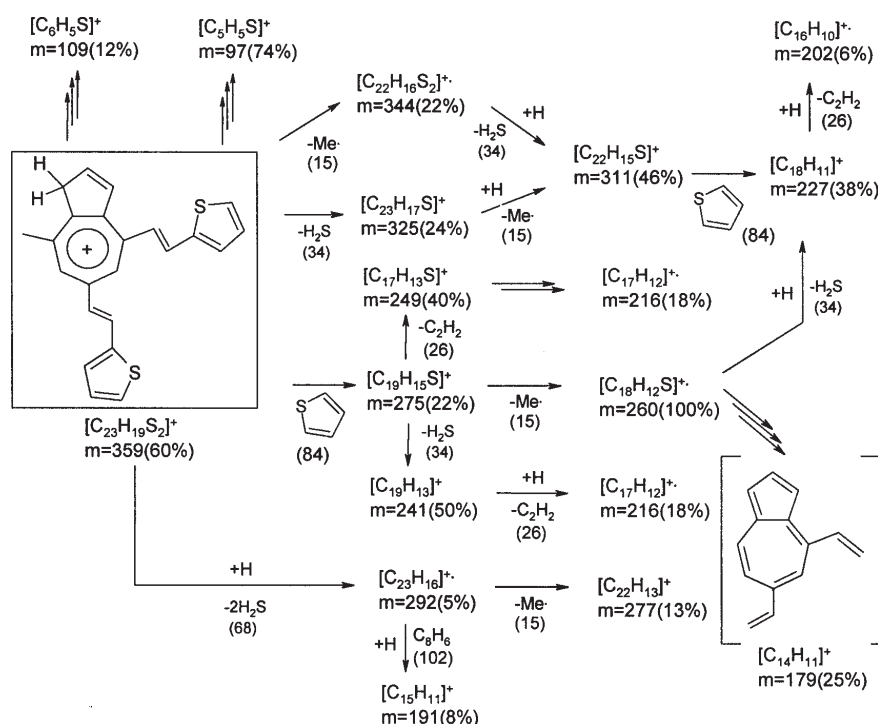
Scheme 4



Owing to the presence in the azulene of more than one methyl able to condensate with thiophene derivatives, together with the above analyzed compound, the double condensation product, bis 4,6-{2-[(*E*)-thien-2-yl]vinyl}-8-methylazulene was obtained. The behaviour of this compound in mass spectrometer necessitates a little attention. Here, the loss of sulphur containing molecules, H_2S and $\text{C}_4\text{H}_4\text{S}$ occurs successively and the succession can be inverted depending on the adopted route (scheme 6). The elimination of two molecules of H_2S is also possible.

An interesting aspect consists in the splitting of the neutral fragment C_8H_6 ($m = 102$) which seems to be phenylacetylene.

As it was discussed above, along with the unsaturated products, at the condensation of alkyl-azulenes with thiophene derivatives, compounds with propane chain were also obtained. The fragmentation of these compounds begins with the splitting of saturated chain, as represented in scheme 7. The obtained cation followed the same routes as for the cation generated in mass spectrometer from the corresponding unsaturated compound.



Conclusions

The above presented data and discussions are consistent with several general rules for the fragmentation of azulenes substituted with alkyl and vinylthienyl groups. Thus, the alkyl groups are eliminated in the known ways as for other alkylated aromatics. The vinylthienyl group however, can be split on several routes. The H_2S and thiophene elimination produces the fragments with the higher abundance. The generation of stable cation $\text{C}_5\text{H}_3\text{S}^+$ or of cation $\text{C}_6\text{H}_3\text{S}^+$ also occur in the mass spectrometer. The chain of saturated compounds analyzed is split in an unsaturated protonated

species that adopts the same fragmentation routes as the same species obtained on the other route.

References

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