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## Mass Spectral Fragmentation Study of Substituted 1,3-Diphenyl-2-pyrazolines II.

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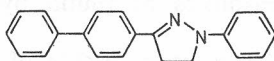
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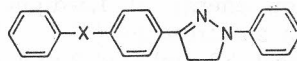
The electron impact induced fragmentation of four 1,3-diphenyl-2-pyrazolines substituted in the *para* position of the 3-phenyl with a phenyl, phenoxy, thiophenoxy or benzoyl group was studied by analyzing metastable peaks and by accurate mass measurements. In general, the fragmentation was found to be in accord with that of 1,3-diphenyl-2-pyrazoline. Some characteristic features in their mass spectra are caused by hydrogen migrations and skeleton rearrangements.

The mass spectral behaviour of 1,3-diphenyl-2-pyrazoline (1) and its derivatives mono-, di- and trisubstituted in one or in both phenyl rings with substituents containing no phenyl has been the subject of our previous papers<sup>1,2,3</sup>. In the postulated fragmentation pathway of 1 all the ions in the mass spectrum (except  $m/e$  103) originate from the molecular ion which is the base peak of the spectrum. The results of substituted derivatives compared with those for the parent compound showed that in general phenyl ring substitution does not affect its fragmentation.

In the present paper the study of the influence of substituents containing phenyl on the electron impact induced fragmentation of some 1,3-diphenyl-2-pyrazolines *para* substituted in the 3-phenyl ring included compounds of structures A and B:



A

 $X = O, S, CO$ 

B

In particular, the investigation of compounds of structure B was carried out in order to see if compounds containing O, S or CO between two phenyl rings undergo similar skeleton rearrangement to form a fragment ion of biphenyl structure by dropping a central group such as CO from diphenyl ether and benzophenone<sup>4</sup> or an S atom from diphenyl thioether<sup>5</sup>. The compositions of rearrangement ions were established by exact mass measurements.

The compounds studied were:

1-phenyl-3-(4''-biphenyl)-2-pyrazoline	(Ph-1)
1-phenyl-3-(4''-phenoxyphenyl)-2-pyrazoline	(OPh-1)
1-phenyl-3-(4''-thiophenoxyphenyl)-2-pyrazoline	(SPh-1)
1-phenyl-3-(4''-benzoylphenyl)-2-pyrazoline	(COPh-1)

The relative abundances of the principal ions observed in the mass spectra are presented as bar graphs in Figure 1.

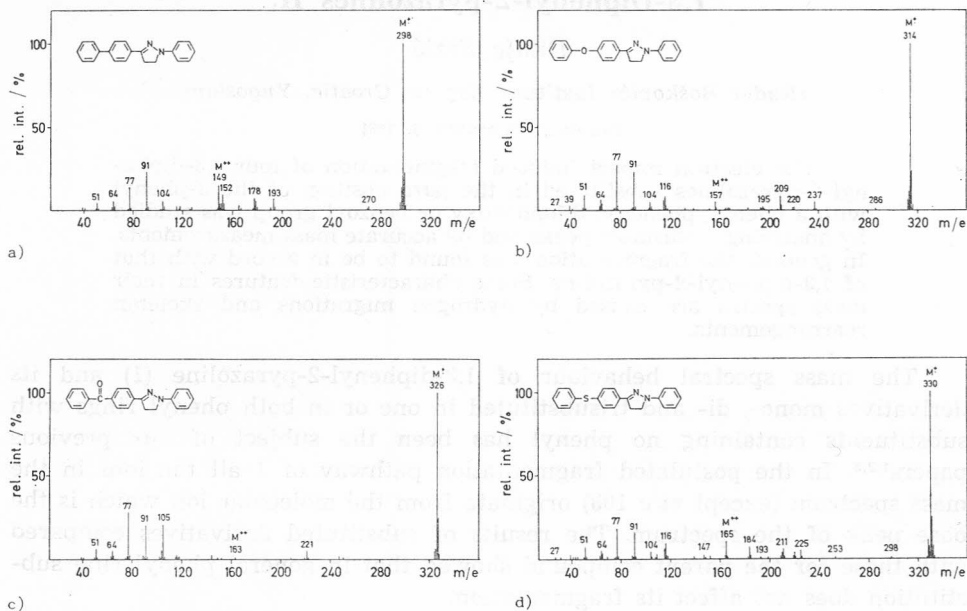


Figure 1. Normalized 70 eV mass spectra of a) 1-phenyl-3-(4''-biphenyl)-2-pyrazoline, b) 1-phenyl-3-(4''-phenoxyphenyl)-2-pyrazoline, c) 1-phenyl-3-(4''-benzoylphenyl)-2-pyrazoline, d) 1-phenyl-3-(4''-thiophenoxyphenyl)-2-pyrazoline

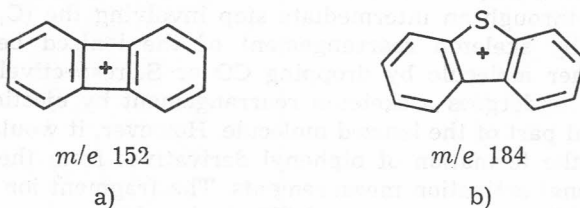
All the compounds appear to be very stable, having the molecular ion as the base peak. The stability to electron impact can be explained by the unusually low ionization energy of 1,3-diphenyl-2-pyrazolines as found by molecular photoelectron spectroscopy ( $< 7$  eV)<sup>6</sup>.

As in most 1,3-diphenyl-2-pyrazolines<sup>1,2,3</sup> the mass spectra of compounds investigated in this study display doubly charged molecular ions  $M^{2+}$ . The relative intensities of  $M^{2+}$  ions in percent as well as their percentage of the total ion currents decrease in the order Ph-1, SPh-1, OPh-1 and COPh-1 from 15%, 10%, 5% to 1%, respectively, and from 5%, 3%, 2% to 0.4%, respectively. As in the unsubstituted benzophenone mass spectrum<sup>4</sup>, the low intensity of the doubly charged  $M^{2+}$  ion in the mass spectrum of COPh-1 might be explained by the low appearance potential of the fragment ion  $[C_6H_5CO]^+$  of  $m/e$  105 in comparison to the second ionizing potential.

The mass spectra of substituted 1,3-diphenyl-2-pyrazolines are generally poor in fragments. The compounds investigated follow the general fragmentation scheme given for the unsubstituted 1<sup>1</sup>. In their mass spectra fragmentation,

being characteristic for the parent compound and yielding ions of  $m/e$  64, 77, 91, 103, 104, 105, 115, 117 and 118, can easily be recognized (see figure 1). However, fragment ions containing 3-phenyl above  $m/e$  ratios are either reduced by 1 or enhanced by (substituent - 1) mass units since two corresponding forms of ions, i. e. an unsubstituted one and one bearing the substituent usually appear in the spectrum.

As was expected the relative abundances of the fragment ions bearing substituent decrease in the same order as the relative abundances of the doubly charged molecular ions. In this connection the relative high intensities of the fragment ions of  $m/e$  152 ( $[C_{12}H_8]^+$ ) and  $m/e$  184 ( $[C_{12}H_8S]^+$ ) containing



two phenyl rings are to be noted in the mass spectra of Ph-1 and SPh-1, respectively. The  $m/e$  152 ion might have a biphenylene structure (a) and the  $m/e$  184 a dibenzothiophene structure (b). The corresponding ions are of small intensity in the mass spectrum of OPh-1 or negligible in the mass spectrum of CPh-1. Moreover, the cleavage of the phenyl-substituent bond as found by second field free region metastables takes place after (for Ph-1 and SPh-1) or parallel to (for OPh-1 and CPh-1) the primary fragmentation of 1, which includes destruction of the pyrazoline ring.

In the mass spectra of 1 and its substituted derivatives studied earlier the direct loss of phenyl from the molecular ion was observed mainly as the ion  $m/e$  77, whereas the corresponding  $[M-C_6H_5]^+$  ion was negligible. On the other hand, substituted 1,3-diphenyl-2-pyrazolines containing phenyl in the substituent, including compounds of structure B, exhibit the  $[M-C_6H_5]^+$  ion. Thus the process giving the  $[M-C_6H_5]^+$  ion must include the elimination of the phenyl from the substituents.

In addition to these common processes a fragmentation yielding  $[M-C_6H_5CO]^+$  and the corresponding  $[C_6H_5CO]^+$  appears to be one of the dominant fragmentation modes in the mass spectrum of CPh-1. The metastables indicate their direct formation from the molecular ion. As was expected the  $[C_6H_5CO]^+$  ion decomposes further with expulsion of carbon monoxide.

A direct loss of phenol and thiophenol from the molecular ion is observed in the mass spectra of OPh-1 and SPh-1, respectively. Thus, a hydrogen migration must be postulated for their formation.

Mass spectrometric investigation shows that diphenyl ether, benzophenone and diphenyl thioether upon dissociation by electron impact undergo a skeleton rearrangement<sup>4,5</sup>. The series of rearranged ions observed in their mass spectra are presumably formed by rearrangement and simultaneous ejection of the central part of the molecule as neutral product(s).

One of the main fragment ions in the mass spectrum of phenyl ether is the rearranged ion of  $m/e$  142,  $[C_{11}H_{10}]^+$  formed by loss of CO from the

molecular ion<sup>4</sup>. A direct loss of carbon monoxide from the molecular ion in the mass spectrum of OPh-1 is not observed. On the basis of exact mass determination the weak intensity ion of  $m/e$  286 is formed by loss of  $C_2H_4$  from the molecular ion. However, the composition  $[C_{11}H_9]^+$  of the ion at  $m/e$  141 corresponds to a skeleton rearrangement. This ion of presumably benzotropylium structure is formed, as indicated by second free field metastables, by dropping CO from the benzophenyl ion originating from the molecular ion.

Benzophenone and diphenyl thioether show a series of rearranged ions corresponding to biphenyl of  $m/e$  154 and its fragment ions<sup>4,5</sup>. It thus appears that a series of decomposition processes of these compounds under electron impact proceed through an intermediate step involving the  $[C_{12}H_{10}]^+$  ion. This ion is formed by skeleton rearrangement of the ionized benzophenone or diphenyl thioether molecule by dropping CO or S, respectively. In the same way SPh-1 also undergoes a skeleton rearrangement by ejection of a S atom from the internal part of the ionized molecule. However, it would be interesting to substantiate the formation of biphenyl derivatives from the diphenyl thioether by collisional activation measurements. The fragment ion  $[C_{12}H_8]^+$  of  $m/e$  152 observed in the mass spectrum of SPh-1 also shows up as the rearranged ion in the mass spectrum of COPh-1. Thus electron impact induced decomposition of CPh-1 also proceeds through an intermediate step involving the skeleton rearrangement by dropping CO.

#### EXPERIMENTAL

The low resolution mass spectra were recorded using a Varian CH-7 instrument operating at 70 eV, 100  $\mu$ A and 3 kV. The accurate mass determinations by the peak matching technique were made on a CEC 21-110C instruments at the »Jožef Stefan« Institute, Ljubljana, Yugoslavia. All samples were introduced into the ion source by the direct insertion method.

Substituted 1,3-diphenyl-2-pyrazolines were prepared by reaction of the corresponding substituted  $\beta$ -dimethylaminopropiophenone hydrochloride (Mannich's base) with phenylhydrazine<sup>7</sup>. Details on their characterization, purity and spectral data are given in Ref. 8.

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**SAŽETAK****Studij fragmentacije supstituiranih 1,3-difenil-2-pirazolina spektrometrijom masa II***D. Srzić*

Fragmentacija četiri 1,3-difenil-2-pirazolina supstituiranih u *para* položaju 3-fenila s fenil, fenoksi, tiofenoksi ili benzoil grupom do koje dolazi nakon bombardiranja s elektronima, studirana je analizom metastabilnih iona i određivanjem točnih masa. Rezultati uspoređeni s podacima za nesupstituirani spoj pokazuju da se supstitucijom fenila ne mijenja osnovna fragmentacija. Karakteristični ioni prisutni u njihovim spektrima nastaju kao posljedica premještanja vodika i pregrađivanja skeleta molekula.

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