J. Chem. Soc. Pak. Vol. 4, No. 2, 1982.

Mass Spectra of NN-Linked Bi(Pyridones) and Their Isomeric Pyrans

AMIR SULTAN AFRIDI
Department of Chemistry, Government Postgraduate Jehanzeb College Saidu-Sharif, Swat.

(Received 27th October, 1980)

Summary: A mass spectral fragmentation study for a number of NN-linked bi(pyridones) (V-VIII) has been carried out. The effect of substituents at the 2-, 4- and 6-position for these heterocycles have been investigated. The isomeric structures VIII and IX might reasonably be expected to exhibit i.r. and n.m.r. spectra bearing some similarity to each other. The differentiation between the isomeric structures VIII and IX was achieved by mass spectrometry. Whereas the molecular ions ($M^{\cdot +}$) give fragment ions ($M^{\cdot +}$ -CO) due to the loss of the C=O groups at the 2- and 4-positions, daughter ions $R\text{-}C{\equiv}N^{\cdot +}$ and $R\text{-}C{\equiv}O^{+}$ are obtained for 6-substituted pyridones and pyrans respectively.

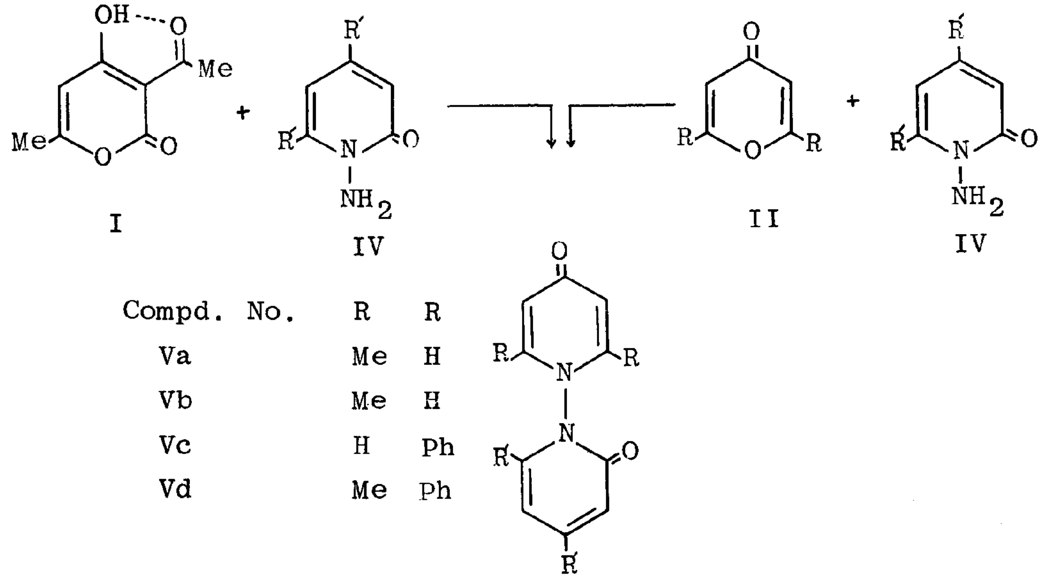
Introduction

Although NN-linked bi(pyridones) are potentially useful as synthetic intermediates, only a few compounds belonging to type (V and VII) have been reported.[1,2] Our previous studies[3,4] have shown tht 1-amino-2-pyridones(IV)[5,6] in hot pyridine react with dehydroacetic acid (I)[7] or with 4-pyrones (II)[8] giving NN-linked bi(2,4-pyridones) of tupe Va-d) (Scheme I). Similarly NN-linked bi(4-pyridones) (VIIa-c) can be prepared from dehydroacetic acid (I) and 4-pyrones (II) with 1-amino-4-pyridones (VI) and hydrazine hydrate (Scheme II).

We have found that while 4-pyrones (II, and 1-aminopyridones (IV and VI hot pyridine gave NN-linked bi(pyridones) (V-VII), the isomeric 2-pyrones (III) upon reaction with N-aminoteterocycles in phosphoryl chloride provided instead of the expected NN-linked bi(hectercycles) (IX), the isomeric pyran derivatives (VIII)[10] (Scheme I . In our previous studies, we have reported the preparation of these compounds (V-VIII). The present study deals wit the mass spectra of NN-linked bi(Pyridones)(V-VII)(Scheme IV) and pyrans(VIII) Scheme V).

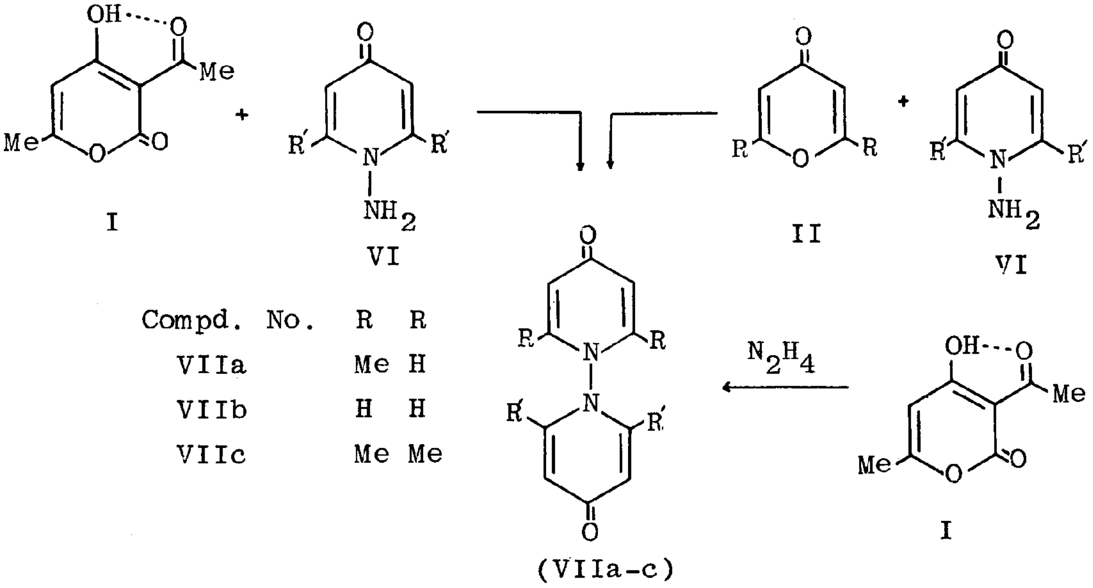
Materials and Methods

Preparation of NN-linked bi-(2,4-pyridones) Va-d) (Scheme I). Dehydroacetic acid (I) (0.01 mole) and 1-amino-2-pyridones (IV) (0.01 mole) in pyridine (20 ml) were heated under reflux (8-12 h). The solid

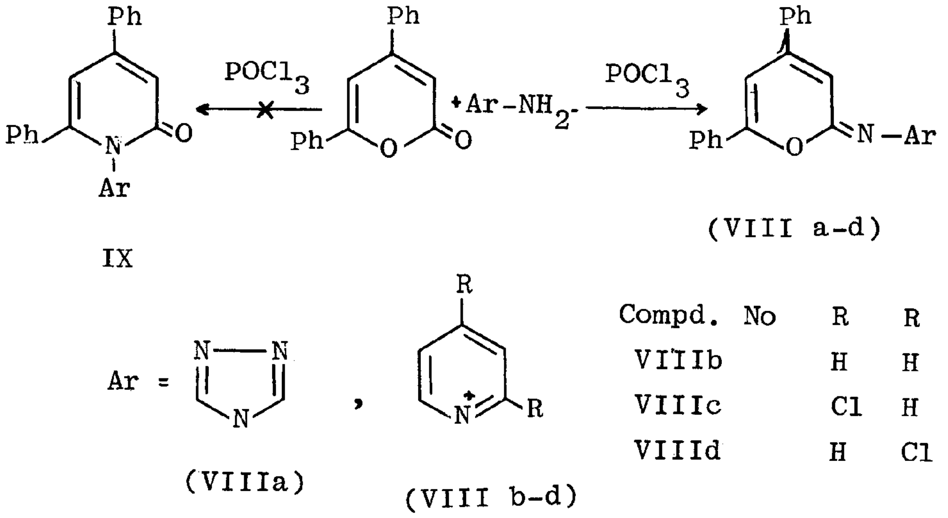


Compd. No.	R	R
Va	Me	H
Vb	Me	H
Vc	H	Ph
Vd	Me	Ph

(Va-d)
Scheme I



Scheme II



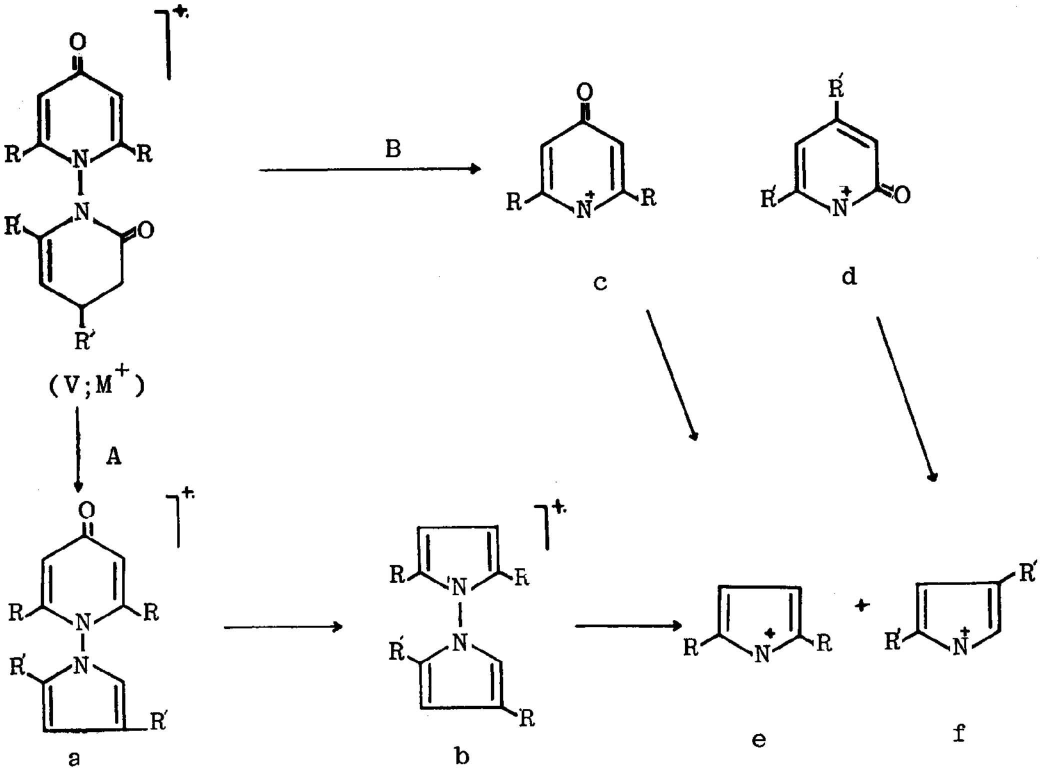
Scheme III

which separated upon cooling, was recrystallised from ethanol and then mixed with 50% aqueous HCl (20 ml). The reaction mixture was heated under reflux (12 h). Evaporation of the solvent and recrystallisation of the residue from 50% aqueous ethanol gave NN-linked bi-(2,4-pyridones) (Va-d).

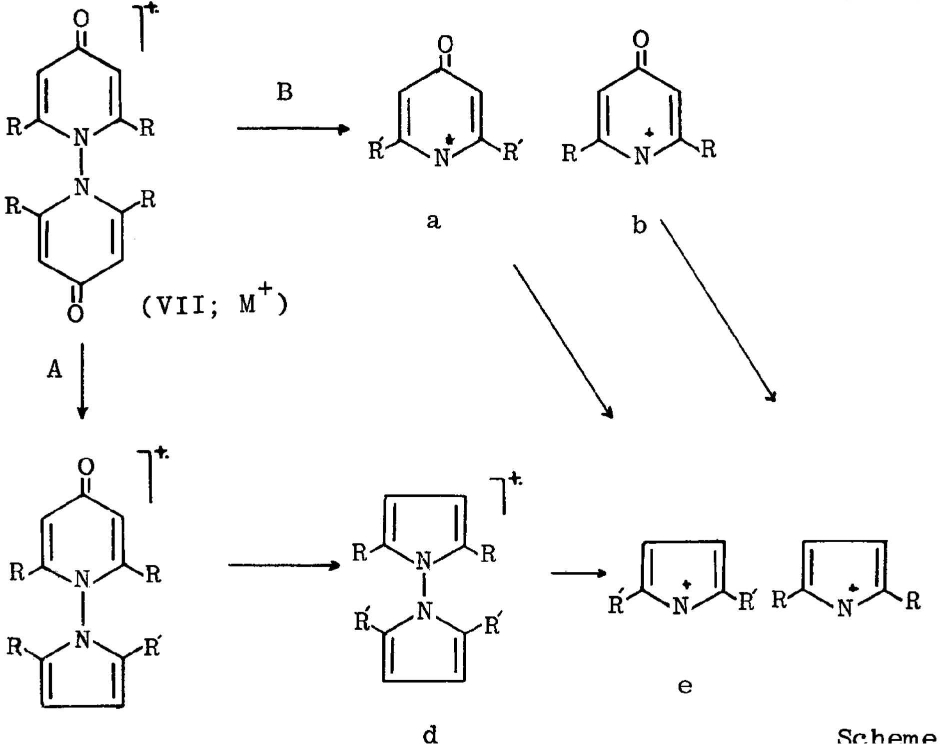
Preparation of NN-linked bi-(4-pyridone) VIIa) (Scheme II).- Using the above method dehydroacetic acid (I) (0.01 mole) and 1-amino-4-pyridone (VI; R′=H) (0.01 mole) gave NN-linked bi-(4-pyridone) (VIIa; R=CH_3, R′=H).

Alternatively, 4-pyrones (II) (0.01 mole) and 1-amino-4-pyridones (VI) (0.01 mole) in pyridine (20 ml) at reflux temperature (24 h) also gave NN-linked bi-(4-pyridones) (VIIz-b).

In a similar sequence using 4-pyrones (II) and 1-amino-2-pyridones (IV) gave NN-linked bi(2,4-pyridones (Va-d) (Scheme I).



Scheme IVa



Scheme IVb

Mass Spectra of compounds Vc, VIIb, VIIIa

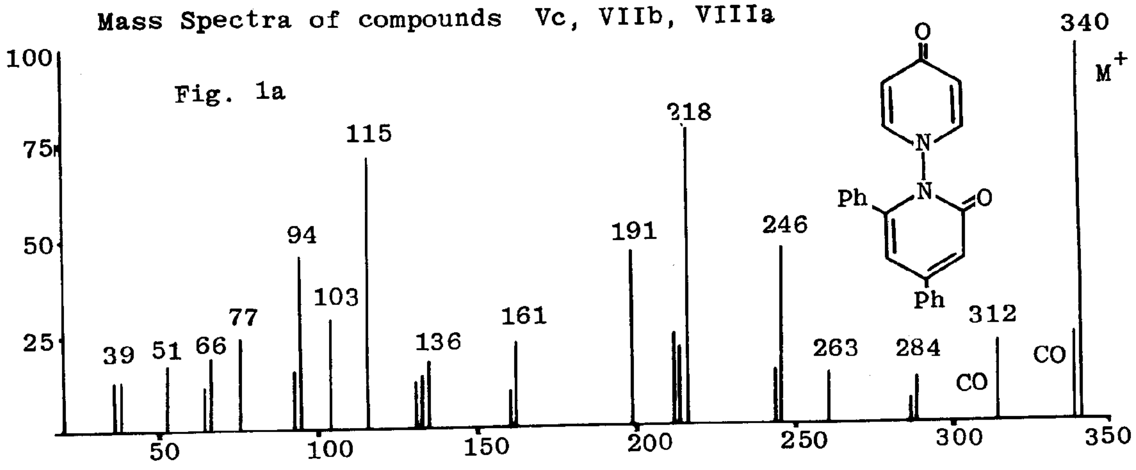


Fig. 1a

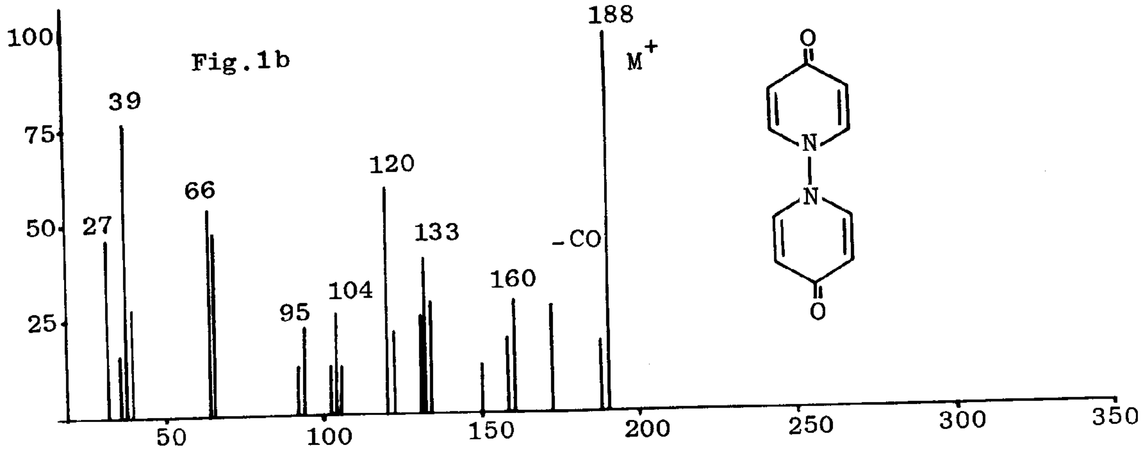


Fig.1b

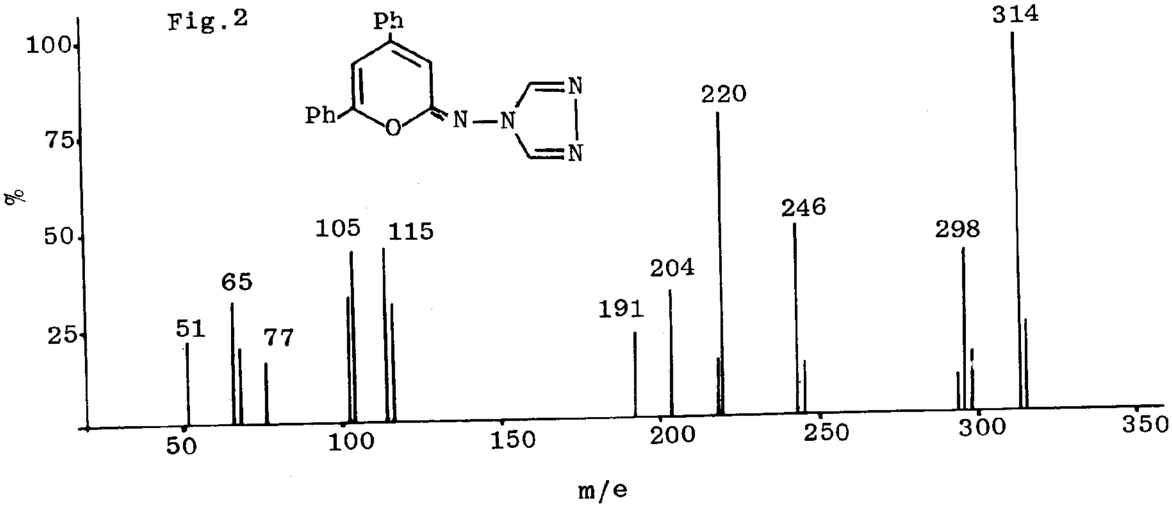
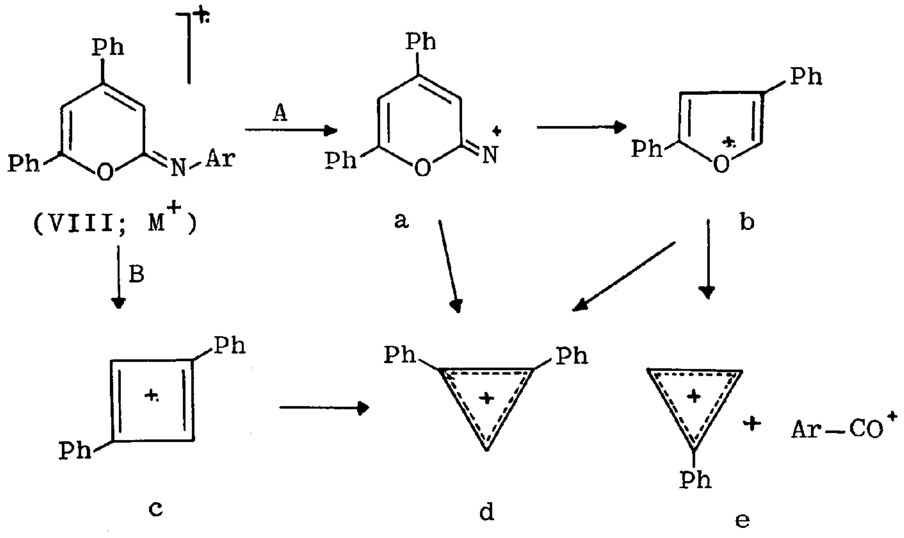


Fig.2



Scheme V

Preparation of NN-linked bi(Lutidones) (VIIc. R= R=CH_3) (Scheme II).- Dehydrocacetic acid (I) (0.05 mole) and hydrazine hydrate (0.025 mole in pyridine (20 ml) were stirred at room temperature (1 h). The solid product was collected and mixed with 50% aqueous Hcl (20 ml). The reaction mixture was heated under reflux (12 h) and the solvent was evaporated. The residue was mixed with 50% equeous pyridine (20 ml) and stirred at room temperature (1 h). Chloroform (25 ml) and water (25 ml) was added and the chloroform extract was evaporated. The residue on recrystallisation from ethanol gave NN-linked bi(lutifone) (VIIc).

Preparation of 2-arylimino-4,6-diphenylpyranes (VIIIa-d) (Scheme III).- 4,6-Diphenyl-2-pyrone (III) 0.01 mole) and 4-amino-1,2,4-triazole (0.01 mole) in phosphory chloride (15 ml) were heated under reflux (4 h). After cooling, ether (50 ml) was added and the solid was washed with ether over filter paper (3x30 ml). The solid was recrystallised from ethanol and identified as compound (VIIIa).

In a similar sequence using 4,6-diphenyl-2-pyrone (III) and 1-aminopyridinium salts, (Scheme III), compounds (VIIIb-d) were obtained.

Results and Discussion

The mass spectra of seven related NN'-linked bipyridones (V-VII) and 2-aryliminopyranes (VIII) are discussed in terms of a general fragmentation scheme IV and V. Accurate mass measurements gave the elemental compositions of ions, but the structures drawn for fragment ions are intended to represent constitutions rather than molecular geometries. Peaks of intensities less than 10% of that of the base peak have been neglected except in cases of special significance.

The fragmentation patterns of the NN-linked bipyridones (V) and (VII) (Scheme IVa,b) are simple. They show molecular ion $M^{\cdot +}$ which apparently fragment by two major pathways (A) and (B). Pathway A gives the fragment ions (a;$M^{\cdot +}$ -CO) and (b; $M^{\cdot +}$ -2CO) which undergo the useal further fragmentation giving the daughter ions (e and f) (Scheme IVa ,b). Pathway B gives the fragment ions (c and d), which then provide the daughter ions (e and f). The fragment ions (e and f) undergo further fragmentation supplying ion R-C=$N^{\cdot +}$.

The mass spectra of the seven related NN'-linked bipyridones (V-VII) are recorded (Table 1) of which that of 4,6-diphenyl-1,1-bi(2,4-pyridone) Vc) and 1,1-bi-(4-pyridone) VIIb) are typical (Figure 1a, b)

The most intense peaks in the mass spectra of the bipyridones (V) and (VII) (Table 1) are usually due to the molecular ion $m^{\cdot +}$ which indicates that the N-N linkage is strong. The low intensities of the fragment ion (a) peaks indicate that these ions have little stability, presumably the observed ion (a) readily loses CO giving the daughter ion (b) peaks.

The fragmentation pattern of pyrans (VIIIa-d) Scheme V) show a strong molecular ion peak $M^{\cdot +}$, which can be regarded a sfragmenting by two major

Table 1. Relative intensities (%) of the principle ions in the mass spectra of NN'-linked bi(pyridones (V and VII).

Compound	R	R'	M^+	a	b	c	d	e	f	$R\text{-}C{\equiv}N^{\cdot+}$
Va	Me	H	100	20	20	100	70	20	100	30
Vb	H	H	100	20	40	30	30	65	65	50
Vc	H	Ph	100	30	20	50	50	25	80	30
Vd	Me	Ph	40	20	15	30	100	15	100	30
VIIa	Me	H	100	35	35	20	20	65	65	50
VIIb	H	H	100	35	35	20	20	65	65	50
VIIc	Me	Me	100	50	80	20	20	60	60	60

Table 2. Relative intensities (%) of the principle ions in the mass spectra of 2-arylimino-4, 6-diphenylpyrans (VIIIa-d).

Compd. No	Ar	M.+	a	b	c	d	e	$Ph\text{-}C{\equiv}CH^{\cdot+}$	$Ph\text{-}C{\equiv}O^+$
VIIIa	1',2',4'-triazolyl	100	55	80	40	30	50	40	50
VIIIb	Pyridinium	100	50	85	30	25	40	30	50
VIIIc	2'-chloropyridinium	80	50	80	40	25	40	20	40
VIIId	4'-chloropyridinium	80	50	80	40	20	40	30	30

pathways (A and B). Pathway A gives the fragment ion (a) due to the loss of Ar^+ from the molecualr ion. Further fragmentation of ion (a) generates the daughter ion (b). Pathway B is associated with the loss of the $Ar\text{-}N{=}C{=}O^{\cdot+}$ fragment providing the daughter ion (c). The fragment ions (a, b and c) undergo the usual further fragmentation giving ions (d and e) along with $Ph\text{-}C{\equiv}O^+$ fragment ion at m/e 105.

The mass spectra of four pyran derivatives (VIIIa-d) are recorded (Table 2) of which that of 4,6-diphenyl-2-(1', 2', 4',-triazol-4'-yl) iminopyran (VIIIa) is typical (Figure 2).

It was observed that the mass spectra of the NN-linked bipyridones (V and VII) (Scheme IVa,b) show daughter ion peads $R\text{-}C{\equiv}N^{\cdot+}$, whereas the pyran derivatives (VIII) (Scheme V) are associated with ion $Ph\text{-}C{\equiv}O^+$ (m/e 105) which is highly diagnostic of the heteroatom in thering. This phenomenon provides a valuable method for distinguishing between the isomeric structural types (VIII) and (IX) (Scheme III).

Acknowledgement

The paper is developed from my Ph.D thesis which I completed at University of East Anglia, Norwich, England. I am thankful to my supervisor, Professor A.R.Katritzky and colleague Dr. C.A. Ramsden for their guidance, encouragement and valuable suggestions. I am also thankful to my Government for the financial support.

References

1. A.R. Katritzky and J.W. Suwinski, Tetrahedron Letters, 4123, 1974; A R.Katritzky and J.W. Suwinski, *Tetrahedron,* 31, 1549, 1975.
2. A.R.Katritzky and M.P. Sammes, *J.C.S. Chem. Comm,* 247, 1975.
3. A.R.Katritzky, A.Sultan Afridi and C.A.Ramsden, *J.Chem Soc. (Perkin Transaction I),* 1428, 1977.
4. A.R. Katritzky, A.Sultan Afridi and C.A.Ramsden, *Pakistan J.Sci. Ind. Res,* Vol. 21, No 1, 1, 1978.
5. R. Gosl and A. Meuwsen, *Chem. Ber,* 52, 2521, 1959; *Angew Chem.* 69, 754, 1957.
6. I.E.S. El-Kholy, M.K. Rafla and M.M. Mishrikey, J. Chem. Soc, 11, 1578, 1970.
7. F. ARndt, B. Eistert, H. Scholz and E. Aron, *Chem. Ber;* 69, 2373, 1936; F. Arndt, *Org. Synthesis,* Coll. Vol. III, 231.
8. R. Willstatter and R. Pummerer, *Ber. Datsch. Chem. Ges,* 37, 3745, 1904.
9. F. Arndt and B. Eistert, *Chem. Ber.* 58, 2318, 1925.
10. A. Sultan afridi, A. R. Katritzky and C.A. Ramsden, *J. Chem. Soc. (Perkin Transaction 1),* 1436, 1977.