Electron Impact Mass Spectrometry of 3-Methyl-4-benzylideneamine-5-styrylisoxazoles. II.

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The mass spectra of a series of substituted 3-methyl-4-benzylideneamine-5-styrylisoxazoles are reported and discussed. The spectra of these isoxazoles show a characteristic fragmentation pattern different from the 5-styryl-4-nitroisoxazoles. Perhaps this is due to the presence of the Schiff base at position 4.

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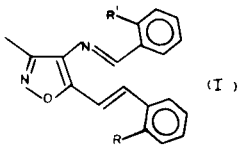
A recent paper (3) has described the behaviour of 3-methyl-6-styryl-4-nitroisoxazoles upon electron impact in which we found that fragmentation patterns are influenced by the nitro group in position 4. As an extension of the work we have examined the spectra of fifteen 3-methyl-4-benzylideneamine-5-styrylisoxazole derivatives of type I (Scheme 1).

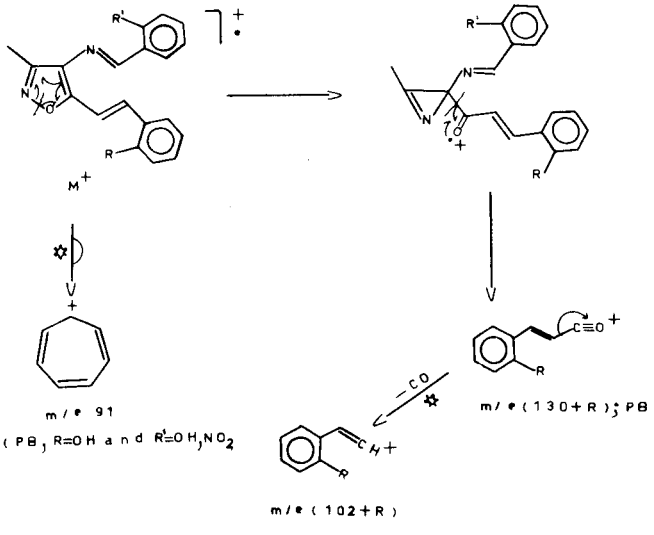


(I)

R = H, Me, OH, Cl, OMe

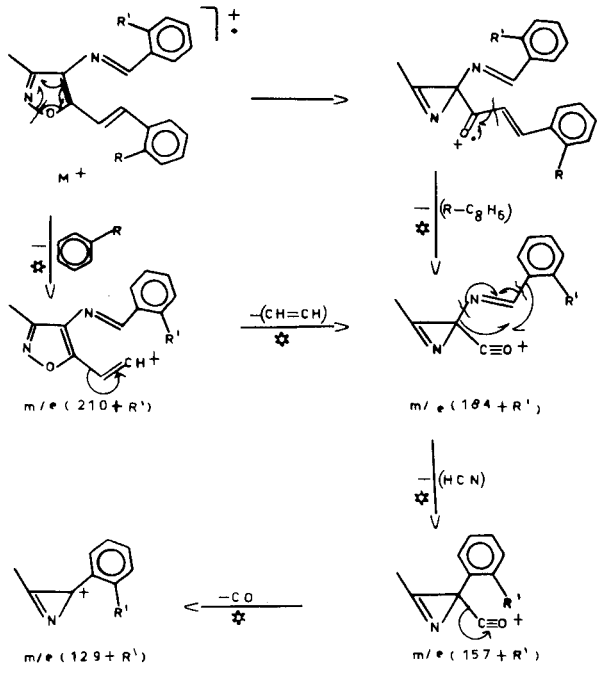
R' = OH, Cl, NO_2

SCHEME 1



SCHEME 2

Most ions in the mass spectrum of these compounds arise from cleavage of the heterocyclic N-O bond in addition to cleavages of the styryl moiety. In the majority of spectra 3-methyl-4-benzylideneamine-5-styrylisoxazoles, a characteristic fragment at m/e (130 + R) is observed which originates by α-cleavage of the azirine carbonyl



SCHEME 3

function in the molecular ion (4). The existence of this species makes the identification of I a relatively easy matter. This ion then loses carbon monoxide resulting in m/e (102 + R). Fragmentation of this last ion is dependent on the R-substituents. When R = OH and R' = OH or NO_2, the base peak is an ion at m/e 91; this is an exception to the rule for these compounds (Scheme 2).

Although the ion at m/e (184 + R') [M^+-(R-C_6H_4CH=CH)] is similar to the ion at m/e (M^+-R), mentioned earlier (5), it loses HCN and then CO, yielding an ion at m/e (157 + R') and m/e (129 + R') and not CO as has been described for alkyl and aryl isoxazoles. Another possible pathway for their formation is by loss of acetylene from an ion at m/e (210 + R') (Scheme 3). Another interesting cleavage of the heterocyclic N-O bond is the elimination of 29 (mass units) (CH=O) from the molecular ion, involving one hydrogen atom of the 3-methyl group and a CO from the heterocycle, producing an ion at m/e (M^+ −29). The driving

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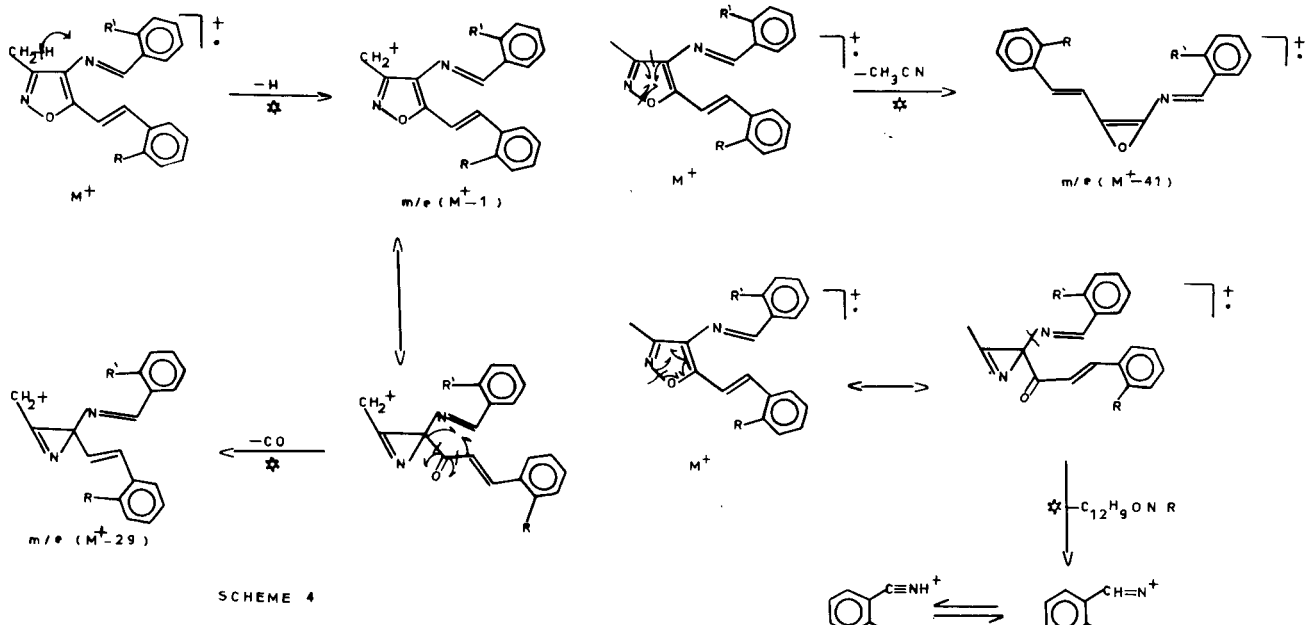
Table I

Analytical and Spectral Data for I

Compound No.	R	R'	M.p. (°C)	Formula	Analysis C	H	N	Ir (Potassium Bromide) Cm^{-1}
1	H	OH	110-112	$C_{19}H_6N_2O_2$	74.98 (74.92)	5.30 (5.28)	9.21 (9.18)	3460 (OH); 1630, 960 (C=C); 760 (*o*-Ar); 1600, 1590 (C=N)
2	H	Cl	117-118	$C_{19}H_{15}ClN_2O$	70.68 (70.70)	4.68 (4.68)	8.68 (8.72)	1640, 950 (C=C); 750 (*o*-Ar); 1590, 1580 (C=N)
3	H	NO_2	140-142	$C_{19}H_{15}N_3O_3$	68.46 (68.40)	4.54 (4.52)	12.61 (12.58)	1630, 960 (C=C); 750 (*o*-Ar); 1600, 1590 (C=N); 1520, 1350 (-NO_2)
4	Me	OH	160-162	$C_{20}H_{18}N_2O_2$	75.45 (75.39)	5.70 (5.68)	8.80 (8.75)	3450 (OH); 1625, 960 (C=C); 760 (*o*-Ar) 1600, 1590 (C=N)
5	Me	Cl	90-91	$C_{20}H_{17}ClN_2O$	71.30 (71.32)	5.08 (5.02)	8.32 (8.30)	1630, 965 (C=C); 760 (*o*-Ar); 1610, 1600 (C=N)
6	Me	NO_2	123-125	$C_{20}H_{17}N_3O_3$	69.15 (69.10)	4.93 (4.89)	12.10 (12.04)	1610, 970 (C=C); 750 (*o*-Ar); 1580, 1590 (C=N); 1348, 1528 (NO_2)
7	OH	OH	235-236	$C_{19}H_{16}N_2O_3$	71.24 (71.20)	5.03 (4.97)	8.75 (8.70)	3400, 3260 (OH); 1630, 970 (C=C); 760 (*o*-Ar); 1600, 1590 (C=N)
8	OH	Cl	215-216	$C_{19}H_{15}ClN_2O_2$	67.34 (67.30)	4.46 (4.50)	8.27 (8.29)	3450, 3200 (OH); 1630, 960 (C=C); 760 (*o*-Ar); 1600, 1590 (C=N)
9	OH	NO_2	212-214	$C_{19}H_{15}N_3O_4$	65.32 (65.40)	4.33 (4.31)	12.03 (12.00)	3400, 3200 (OH); 1630, 970 (C=C); 750 (*o*-Ar); 1610, 1590 (C=N); 1348, 1525 (NO_2)
10	Cl	OH	130-132	$C_{19}H_{15}ClN_2O_2$	67.34 (67.40)	4.46 (4.48)	8.37 (8.31)	3450 (OH); 1620, 970 (C=C); 760 (*o*-Ar); 1600, 1590 (C=N)
11	Cl	Cl	128-130	$C_{19}H_{14}Cl_2N_2O$	63.86 (63.90)	3.95 (4.02)	7.84 (7.82)	1630, 970 (C=C); 760 (*o*-Ar); 1600, 1590 (C=N)
12	Cl	NO_2	146-148	$C_{19}H_{14}ClN_3O_3$	62.03 (61.98)	3.83 (3.85)	11.43 (11.47)	1630, 970 (C=C); 760 (*o*-Ar); 1600, 1590 (C=N); 1340, 1520 (NO_2)
13	OMe	OH	115-117	$C_{20}H_{18}N_2O_3$	71.84 (71.79)	5.43 (5.42)	8.38 (8.34)	3300 (OH); 1640, 960 (-C=C); 750 (*o*-Ar); 1600, 1590 (C=N); 2840, 1250 (OMe)
14	OMe	Cl	114-115	$C_{20}H_{17}ClN_2O_2$	68.07 (68.00)	4.85 (4.80)	7.94 (7.93)	1630, 960 (-C=C); 750 (*o*-Ar); 1600, 1590 (C=N); 2840, 1250 (-OMe)
15	OMe	H	89-91	$C_{20}H_{18}N_2O_2$	75.45 (75.41)	5.70 (5.72)	8.80 (8.83)	1630, 960 (C=C); 750 (*o*-Ar); 1600, 1590 (C=N); 2840, 1250 (-OMe)



SCHEME 4

SCHEME 5

force for such a process is undoubtedly the production of this stable ion (Scheme 4). The formation of the ion at m/e ($M^+ - 41$) involves the elimination of CH_3CN while

cleavage of the C_4-N imine bond (6) results in an ion at m/e (103 + R') (Scheme 5).

When R' = NO_2 the relative abundance of the fragments discussed above is small; only fragments under the base peak have a high relative abundance.

All fragmentation pathways are supported by the corresponding metastable transitions which are depicted by an asterisk in the Figures.

EXPERIMENTAL

Melting points are uncorrect. The ir spectra were recorded on a Perkin-Elmer model 321 Spectrophotometer. The mass spectra were measured on a Hitachi Perkin-Elmer RMU-7H double focusing mass spectrometer using the direct inlet system. The samples were recorded at an ionization chamber temperature of 190°. All compounds were synthesized following reported procedures (7). The ir absorptions and other data concerning new compounds are recorded in Table I. The H^1 nmr data for these compounds are not given due to their insolubility in solvents usually used in H^1 nmr analysis.

REFERENCES AND NOTES

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(2) Contribution No. 541 from Instituto de Química, U.N.A.M.

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