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Characterization of New Diimines of Carbon Suboxide by Tandem Mass Spectrometry

Robert Flammang,* Sophie Laurent, Monique Barbieux-Flammang and Yves Van Haverbeke
Organic Chemistry Department, University of Mons-Hainaut, 19 Avenue Maistriau, B7000 Mons, Belgium

Curt Wentrup*
Department of Chemistry, The University of Queensland, Brisbane, Queensland 4072, Australia

Bis-aryliminopropadiene radical-cations, [ArN=C=C=C=NAr′]$^{+\cdot}$, have been generated by dissociative ionization of isoxazolopyrimidine precursors and structurally characterized by collisional activation mass spectrometry; the corresponding neutral cumulenes have also been produced in neutralization–reionization experiments.

Dissociative ionization of isoxazole precursors has recently allowed the preparation of new classes of heterocumulene radical-cations. In recent publications,[1,2] we have demonstrated that 3-phenylisoxazolopyrimidinone, **1**, cleanly produces phenyliminopropadienone ions, **4**$^{+\cdot}$, upon electron ionization (EI). The atom connectivity was indicated by collisional activation (CA) mass spectrometry. The corresponding neutrals, **4**, were prepared by reducing a beam of fast **4**$^{+\cdot}$ ions in a neutralization–reionization experiment[1] or by flash-vacuum pyrolysis of **1** at 800 °C.

Similarly, phenylisoxazolopyrimidinethione, **2**, has been shown to be a suitable precursor of phenyliminopropadienethione ions, **5**$^{+\cdot}$.[4] Bis-iminopropadiene ions, of general formula RN=C=C=C=NH$^{+\cdot}$, were also prepared by dissociative ionization of 5-amino-4-cyanoisoxazoles.[2]

We now report briefly on the production and identification of new bis-aryliminopropadiene ions, **6**$^{+\cdot}$, by dissociative ionization of several isoxazolopyrimidines, **3** (Table 1).

RESULTS

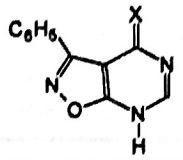
The EI mass spectrum of **3a** (Ar=Ph) features an intense molecular ion peak at *m/z* 288 (Fig. 1). Among the various competitive fragmentations, the loss of 70 u, consisting in the elimination of HCN and HN=C=O, is noteworthy. This reaction is a high-energy process as it is only significantly observed in the ion source or during the flight after CA. This behaviour is thus similar to that of the oxygen or sulfur analogues **1** and **2** which are presently recognized as excellent precursors of heterocumulene radical-cations, **4**$^{+\cdot}$ and **5**$^{+\cdot}$.

The resolved CA spectrum of the *m/z* 218 ions (Fig. 2(a)) shows characteristic peaks at *m/z* 115 (loss of PhN=C) and *m/z* 77 (phenyl cations). The CA (oxygen) spectrum of the *m/z* 115 ions, $C_8H_5N^{+\cdot}$, is very similar to those of the [M − CO]$^{+\cdot}$ and [M − CS]$^{+\cdot}$ ions produced from PhN=C=C=C=O$^{+\cdot}$[1] and PhN=C=C=C=S$^{+\cdot}$[4] ions; it is concluded therefore that the precursor ions also possess the N=C=C=C=N connectivity (Table 2). One significant difference is noted for the intensity of the *m/z* 77 fragment ions. The intensity of this peak decreases rapidly from **4**$^{+\cdot}$ to **6**$^{+\cdot}$. We believe that the $C_8H_5N^{+\cdot}$ ions correspond initially to vinylidene ions, PhN=C=C$^{+\cdot}$, which, depending on the mode of preparation, rapidly isomerize into a new structure which no longer contains an intact phenyl ring and subsequently eliminates HCN. Note that the decreasing intensity of the *m/z* 77 ion peak follows the stability order of the expelled neutrals [ΔH_f°(CO) = −110 kJ/mol, (CS) = 262 kJ/mol, (PhN=C) = 309 kJ/mol].[5]

One characteristic feature of the CA spectra of the *m/z* 115 ions is the occurrence of numerous doubly charged ions which confirm the formation of a common

* Authors for correspondence.

Table 1. Compounds studied

X		$C_6H_5N{=}C{=}C{=}C{=}X$
O	1	4
S	2	5
NC_6H_5	3a	6a
NC_6D_5	3b	6b
$NC_6H_4{-}CH_3(p)$	3c	6c
$NC_6H_4{-}CH_3(m)$	3d	6d

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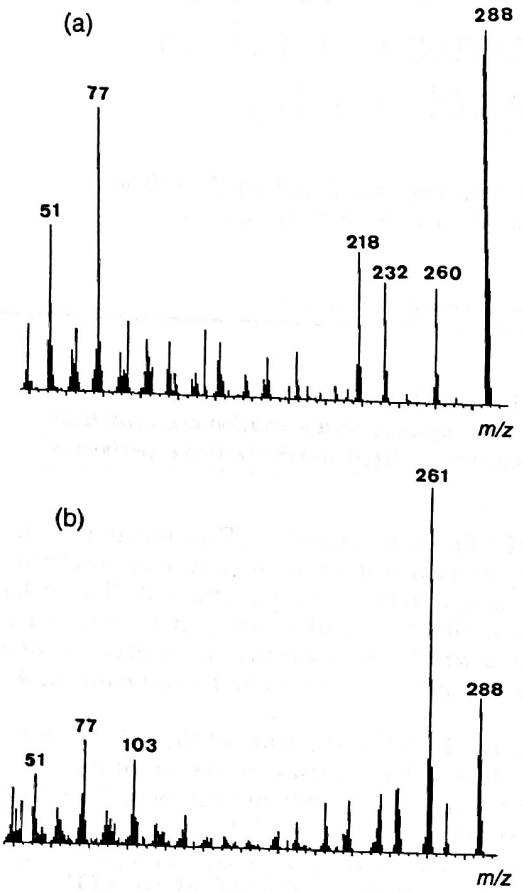


Figure 1. Electron impact mass spectra (70 eV) of the isoxazolopyrimidine **3a** at an oven temperature of (a) 200 °C and (b) 800 °C.

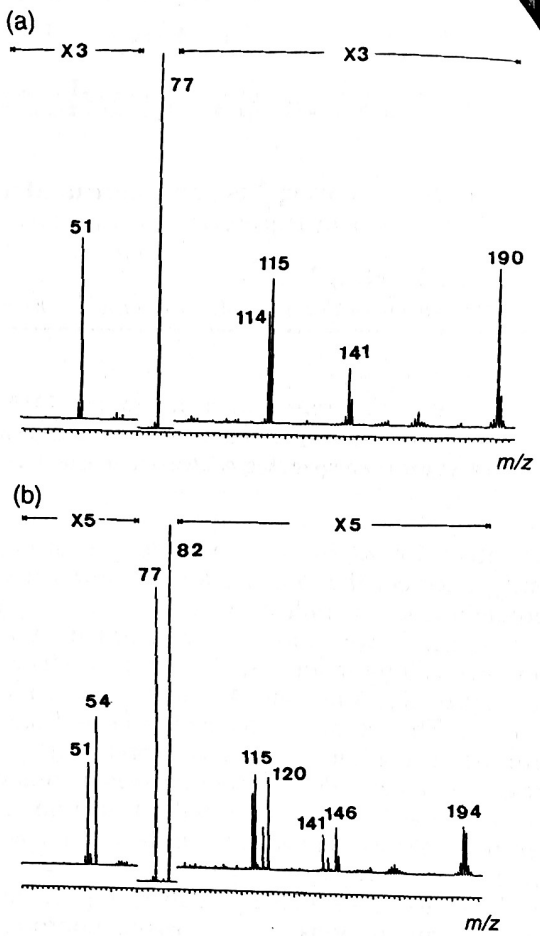
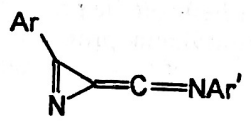


Figure 2. Resolved CA spectra (oxygen) of the *m/z* 218 ions formed by dissociative ionization (a) of **3a** and (b) of the *m/z* 223 ions of the isotopomer **3b**.

structure (Table 3). It is well known that the relative abundances of these ions can be readily used to characterize ion structures.[6]

Further indication of the cumulenic structure $PhN{=}C{=}C{=}C{=}NPh^{1+\cdot}$ is provided by the analysis of the homologues **3c** and **3d**. The CA spectra of the *m/z* 232 ions of these compounds are dominated by two peaks of nearly equal intensities at *m/z* 77 (phenyl cations) and *m/z* 91 (tolyl cations) (Fig. 3). Such behaviour is not expected for isomeric ions like iminomethylene azirine ions $7^{+\cdot}$ which should present a higher specificity in the formation of aryl ions.[7]



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Finally, the study of the isotopomer **3b** supports the previous conclusions, as all the peaks observed in the CA spectrum of the hydrogenated molecule **3a** exhibit the expected splitting for **3b** (compare Fig. 2(a) and 2(b)). The slight preference for the formation of deu-

Table 2. CA (O_2) mass spectra of $C_8H_5N^{+\cdot}$ ions (*m/z* 115) generated by dissociative ionization of isoxazolopyrimidines 1, 2 and 3. Abundances relative to the most intense collision-induced peak. The unimolecular fragmentation already observed without the collision gas is indicated within brackets

Precursors *m/z*	103	100	99	98	[88]	77	75	62	57.5	51	50	39	38	37
$PhNC_3O^{+\cdot}$	3	2	3	1	[294]	55	32	100	7	34	35	14	12	10
$PhNC_3S^{+\cdot}$	1	2	3	2	[294]	21	29	100	8	25	31	14	11	9
$PhNC_3NPh^{+\cdot}$	<1	2	3	2	[255]	8	29	100	6	22	30	15	12	10

Table 3. Charge stripping (CS) mass spectrum of $C_8H_5N^{+\cdot}$ ions (*m/z* 115) generated by dissociative ionization of isoxazolopyrimidines 1, 2 and 3a. Abundances relative to the most intense peak at *m/z* 57.5

Precursors *m/z*	57.5	57	56.5	56	55.5	44.5	44	43.5	43	42.5	42
$PhNC_3O^{+\cdot}$	100	8	28	7	2	7	15	5	19	<1	<1
$PhNC_3S^{+\cdot}$	100	8	21	5	3	7	13	7	15	1	<1
$PhNC_3NPh^{+\cdot}$	100	8	26	6	3	8	15	4	21	<1	<1

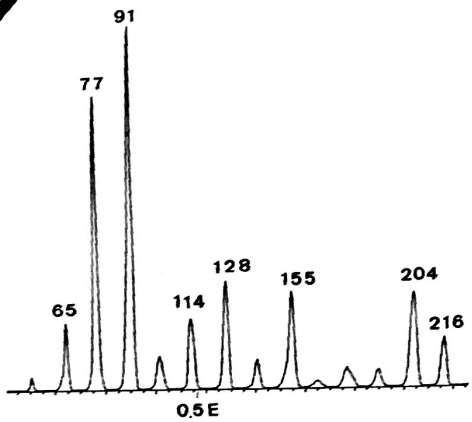


Figure 3. CA (oxygen) mass spectrum of the *m/z* 232 ions generated by dissociative ionization of the methyl homologue **3c**.

terated ions is presently not well understood; one possible explanation could invoke a non-ergodic behaviour.[8]

Figure 4(a) shows the neutralization–reionization (NR) mass spectrum of the *m/z* 218 ions generated from **3a**. This spectrum, obtained after neutralization with ammonia and reionization with oxygen, is characterized by a small but significant recovery signal at *m/z* 218 corresponding to survivor ions, thus indicating the stability of the neutral cumulene, PhN=C=C=C=NPh, **6a**, in the rarefied gas phase of the mass spectrometer.

The spectral modifications observed when ammonia is replaced by dimethylamine in the neutralization cell are worth noting (Fig. 4(b)). The recovery signal disappears almost completely, while the peaks at *m/z* 141, 127 and 103 show a significant intensity increase. The lower ionization energy of dimethylamine (8 eV) relative to ammonia (10 eV)[5] results in an exothermicity increase in the neutralization step which may be high enough to fragment the neutrals into radicals. It is also possible that the relative reionization efficiency of PhN=C=C=C=N$^{\bullet}$ radicals formed by collisional activation is increased by using dimethylamine. The PhN=C=C=C=N$^{\bullet}$ radicals are isoelectronic with O=C=C=C=N$^{\bullet}$ and S=C=C=C=N$^{\bullet}$ radicals identified in NR mass spectrometric experiments on **4**$^{+\bullet}$ and **5**$^{+\bullet}$ ions.[1,4]

We have recently shown that the isoxazolopyrimidinone, **1**, upon flash-vacuum pyrolysis (FVP) at 800 °C, undergoes mainly fragmentation into the propadienone, **4**. Isomerization of the isoxazole ring into oxazole was also observed to a lesser extent.[1] We therefore investigated the FVP behaviour of **3a** using three different sets of conditions: (a) real-time analysis of the pyrolyzate using EI-MS, (b) real-time analysis with chemical ionization (CI)-MS and (c) semi-preparative trapping experiments.

Figure 1(b) shows the mass spectrum of **3a** after

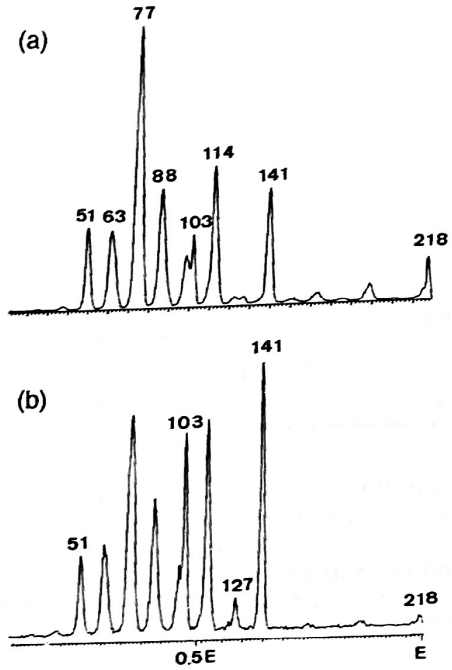


Figure 4. Neutralization–reionization mass spectra ((a) NH_3/O_2 and (b) $NHMe_2/O_2$) of the *m/z* 218 ions generated by dissociative ionization of **3a**. The masses shown are only indicative (overlapping peaks).

flash-vacuum pyrolysis at 800 °C. The main spectral modifications are seen for the *m/z* 261, 232 and 218 ions. That the structure of the remaining *m/z* 288 molecular ions has changed is clearly indicated by the strong modifications observed in their CA spectrum (Table 4). By analogy with the behaviour of the pyrimidinone, **1**, we thus propose the isomerization of **3a** into the oxazolopyrimidine, **7**; such systems are known to lose predominantly HCN by fragmentation of the pyrimidine ring.[1]

In order to facilitate the detection of the molecular ions in the pyrolyzate, we have also applied on-line chemical ionization using methanol as the reagent gas (FVP/CI-MS) and the resulting CI mass spectrum is shown in Fig. 5. Surprisingly, the pyrolyzate appears much more complex than expected on the basis of the EI mass spectrum. Protonated molecules are now observed at *m/z* 289, 246, 219 and 207. These findings were confirmed by semi-preparative pyrolysis experiments where a few milligrams of **3a** were vaporized through an alumina pyrolyzer heated at 750 °C. The pyrolyzate, collected on a liquid-nitrogen-cooled receptor was rapidly dissolved into methanol before reaching room temperature and subsequently analyzed by electron-ionization tandem mass spectrometry (EI-MS/MS). This experiment has allowed the identification of the oxazolopyrimidine, **8** [MW 288], a supposed diphenylcyanopyrazole, **9** [MW 245, thermal loss of HN=C=O], and PhC(CN)=NPh, **10** [MW 206] identi-

Table 4. Resolved CA(O_2) mass spectra of the molecular ions of 3a (*m/z* 288) at 200° and after FVP at 750°. Peaks smaller than 10% of the base peak and loss(es) of hydrogen(s) not included

T(°C)	*m/z*	261	260	259	233	232	231	218	217	205	190	180	157	105	104	103	77
200		100	75	14	21	69	12	69	23	17	10						40
750		100	35	13	29	20				12		54	27	11	10	11	23

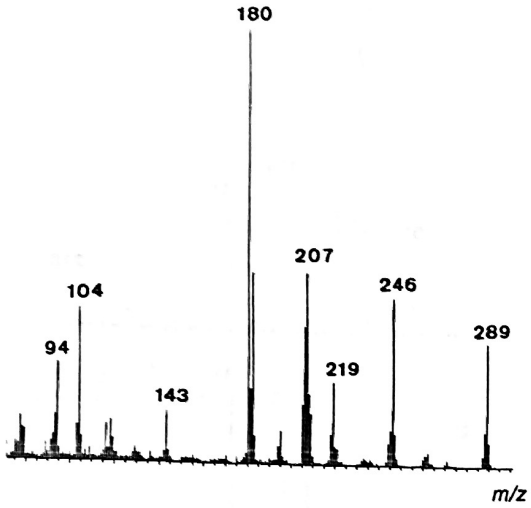
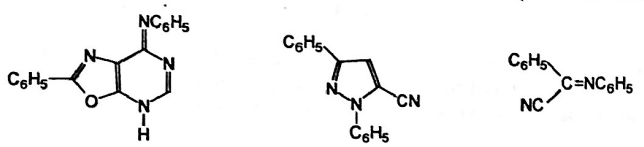


Figure 5. FVP/CI-MS of the isoxazolopyrimidine **3a**; methanol reagent gas, 750 °C oven temperature.

fied by comparison with an authentic sample.[9] Trapping products of **6a** with methanol were *not* observed; moreover, the ions observed at *m/z* 218 (219 in the



8 **9** **10**

CI spectrum) do *not* correspond to $\mathbf{6a}^{+\cdot}$ as their CA spectrum displays no peak at *m/z* 77. Further work is in progress to identify more accurately the components of the pyrolyzate of the pyrimidines **3a–d**.

EXPERIMENTAL

The electron impact mass spectra were recorded on a large scale six-sector VG AutoSpec 6F spectrometer (VG Analytical, Manchester, UK) of $E_1B_1E_2E_3B_2E_4$ geometry (E stands for electric sector and B for magnetic sector) at an accelerating voltage of 8 kV.[10] In the CA experiments, a beam of ions is selected by the combination of the three first sectors ($E_1B_1E_2$) and submitted to collisional activation with oxygen (80% transmittance). In the NR experiments, neutralization of the ions with an appropriate collision gas (80% transmittance) precedes reionization with oxygen, unreacted ions being eliminated by floating the intermediate ion source inserted between the two cells at 9 kV. The distance between the cells is *ca.* 10 cm. The two kinds of spectra were recorded by scanning the field of the third electric sector and collecting the ions in the 4th field-free region with an off-axis photomultiplier detector. The 'resolved' CA spectra were obtained by linked scannings of the last three sectors and collecting the ions at the final detector.

Chemical ionization mass spectra were obtained using methanol (3 μL injected in the septum inlet) as the reagent gas.

The FVP device consists of a quartz tube installed in the source housing of the spectrometer. Details have been described elsewhere.[11] Semi-preparative experiments were performed using a similar pyrolysis device.[1]

The isoxazolopyrimidines **3a–d** were prepared according to the following general procedure: a solution of 5 mmol of 5-amino-4-cyano-3-phenylisoxazole prepared according to the Literature,[14] in 15 mL of triethyl orthoformate was refluxed for 7 h in the presence of a small amount (0.5 mL) of acetic anhydride. After concentration *in vacuo*, the residual oil was mixed with a small excess of a primary aromatic amine in dry methanol and boiled for 7 h. On cooling, the pyrimidine precipitated and was recrystallized in methanol.

3a (m.p. 144–146°, 70%); PMR (300 MHz, DMSO-d_6) 8.7 (1H,s,C_6H), 8.7 (1H,broad,NH) 8–7.9 (2H,m,Ph), 7.75–7.65 (3H,M,Ph), 7.6 (2H,d,Ph), 7.4 (2H,t,Ph), 7.2 (1H,t,Ph); MS: 288.0992

3b (m.p. 147–149°, 74%); PMR: 8.7 (1H,s,C_6H), 8.7 (1H,broad,NH), 8–7.9 (2H,m,Ph), 7.75–7.65 (3H,m,Ph)

3c (m.p. 178–179°, 70%); PMR: 8.7 (1H,s,C_6H), 8.7 (1H,broad,NH), 8–7.9 (2H,m,Ph), 7.75–7.65 (3H,m,Ph), 7.5–7.2 (4H,AA'BB'), 2.3 (3H,s,CH_3); MS: 302.1186

3d (m.p. 133–135°, 88%); PMR: 8.7 (1H,s,C_6H), 8.7 (1H,broad,NH), 7.95–7.85 (2H,m,Ph), 7.75–7.65 (3H,m,Ph), 7.4 (2H,m,Tol), 7.3 (1H,t,Tol), 7.0 (1H,d,Tol), 2.3 (3H,s,CH_3); MS: 302.1166

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