Imides: Part VIII* - Pyrolysis and Pyrolysis-Mass Spectra of N-Hydroxy-Cyclohex-4-Ene-1,2-Dicarboximide and its Derivatives

N.F.ALY, S.A.ESSAWY**, M.O.ORABI***
AND N.Y.ALY
Department of Chemistry, Faculty of Science, Ain Shams University, Abbasia, Cairo, Egypt.

[Received 18th August, 1985]

Summary: N-Hydroxy-, N-aroyloxy-, and N-arylsulphonyloxy-cyclohex-4-ene-1,2-dicarboximides (I,IV and VI) undergo pyrolysis to give phthalimide (II); mixture of (II), aromatic acids; and mixture of (II), arylsulphonic acids, respectively. N-aryl-cyclohex-4-ene-1,2-dicarboximides (VIII) give on pyrolysis N-aryl-phthalimides (IX). Pyrolysis-mass spectra of (I), (IVa) and (VIa) was investigated.

It was previously [3] stated that N-hydroxy-phthalimide, and its derivatives give on pyrolysis phthalimide. In the present investigation pyrolysis and pyrolysis-mass spectra of N-hydroxy-cyclohex-4-ene-1,2-dicarboximide and its derivatives were investigated.

Results and Discussion

I. Pyrolysis:

N-Hydroxy-cyclohex-4-ene-1,2-dicarboximide (I) gives on pyrolysis phthalimide (II) via N-hydroxy-phthalimide (III). N-aroyloxy-cyclohex-4-ene-1,2-dicarboximide (IVa-c) give on pyrolysis mixtures of (II) and the corresponding aromatic acids via N-aroyloxy-phthalimides (V). Similarly N-arylsulphonyloxy-cyclohex-4-ene-1,2-dicarboximides (VIa,b) give an pyrolysis mixtures of (II), and the corresponding arylsulphonic acids, via N-arylsulphonyloxy-phthalmides (VII).

The reaction probably takes place according to Scheme-1.

Structure of (II), and arylsulphonic acids was proved by m.m.p. determination with authentic samples [3].

The above scheme was confirmed from the fact that:

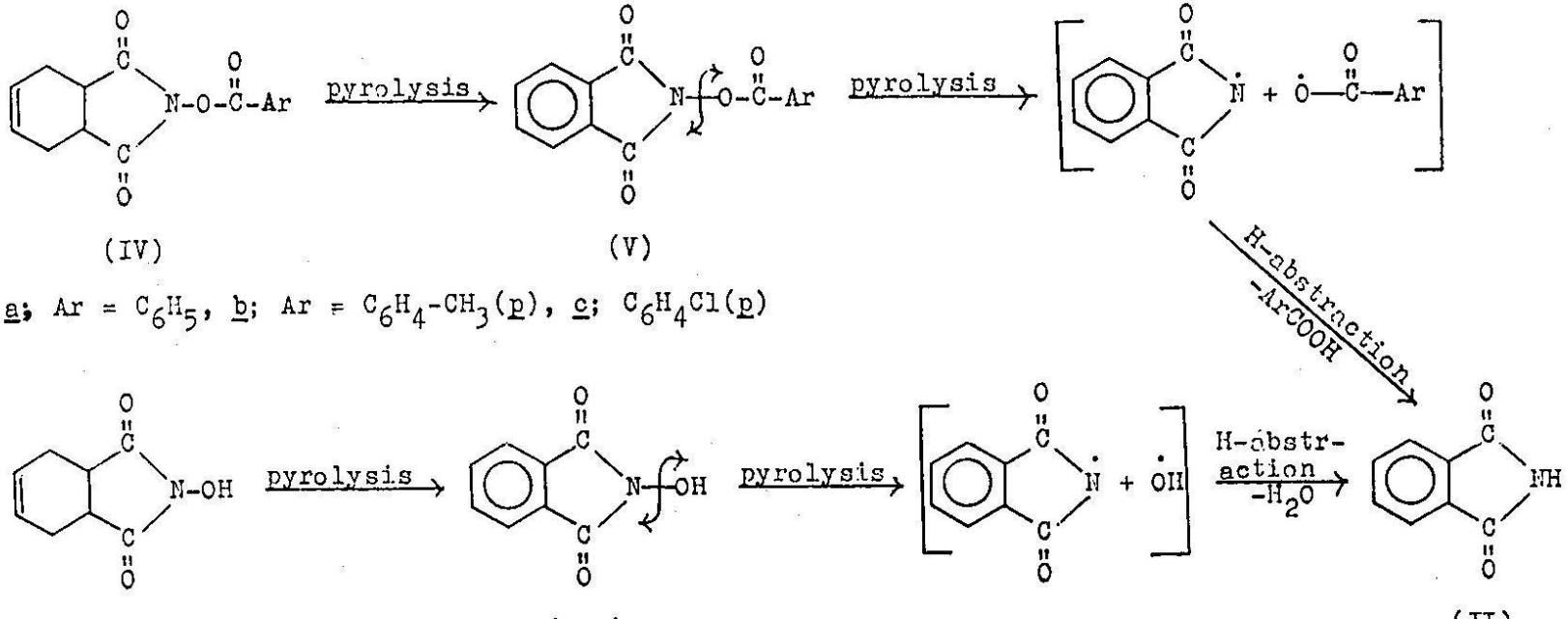
i) Heating of N-hydroxy-cyclohex-4-ene-1,2-dicarboximide (I) above its m.p. gives N-hydroxy-phthalimide (III), which gives on pyrolysis phthalimide (II) [3].

ii) Heating of N-aroyloxy-cyclohex-4-ene-1,2-dicarboximides (IVa-c) above their m.ps. gave N-aroyloxy-phthalimides (Va-c) which give on pyrolysis phthalimide (II) and aromatic acids [3].

iii) Heating of N-aryl-sulphonyloxy-cyclohex-4-ene-1,2-dicarboxyimides (VIa,b) above their m.ps. gave N-aryl-sulphonyloxy-phthalimides (VIIa,b) which give

* Part I-VII of this series, see refs.1-7 respectively.

** Faculty of Science, Benha University.
*** Faculty of Science, Suez Canal University.



(IV) (V)

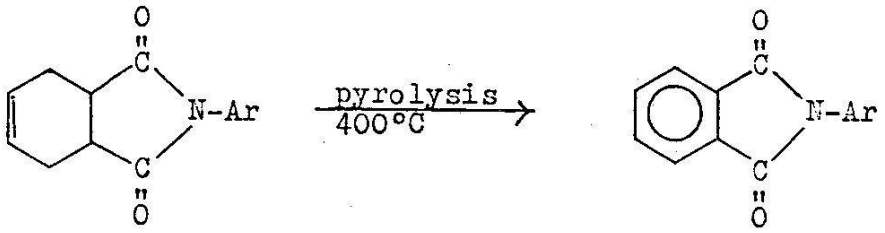
a; Ar = C_6H_5, b; Ar = C_6H_4-CH_3(p), c; C_6H_4Cl(p)

(I) (III) (II)

(VI) (VII)

a; Ar = C_6H_5, b; Ar = $C_6H_4CH_3$(p)

(Scheme I)



(VIII) (IX)

a;Ar=C_6H_5, b; Ar=$C_6H_4CH_3$(p-), c; Ar=$C_6H_4OCH_3$(p-), d;Ar=C_6H_4Cl(p-)

on pyrolysis phthalimide (II), and aryl-sulphonic acids [3].

Similarly pyrolysis of N-aryl-cyclohex-4-ene-1,2-dicarboximides (VIIIa-d) at 400°C gives N-aryl-phthalimides (IXa-d).

Structure of (IXa-d) was proved from m.m.p. determination with authentic samples [4].

II. Pyrolysis-mass spectra:

Pyrolysis-mass spectrum of N-hydroxy-cyclohex-4-ene-1,2-dicarboximide (I):

When N-hydroxy-cyclohex-4-ene-1,2-dicarboximide (I) was introduced in the mass spectrometer via a hot indirect inlet system at (280°C), it gives the pyrolysis stable fragments. The pyrolysis fragmentation pattern showed the following stable compounds via loss of oxygen atom to give cyclohex-4-ene-1,2-dicarboximide (X; m/z 151), which undergoes pyrolytic fragmentation via three routes: (cf. Chart I).

Route (i): Involves fragmentation via (retro-Diels-Alder) reaction to give maleimide (m/z 79) and butadiene (m/z 54).

Route (ii): Involves fragmentation ot isocyanate of cyclohex-1,3-diene (m/z 121), aniline (m/z 39), and carbon monoxide.

Route (iii): Involves aromatization to phthalimide (II) (m/z 147) which gives cyclopentadiene (m/z 66) via a mechanism showed in (chart I).

All the above mentioned compounds showed the expected parent peaks, and mass spectral fragments in the mass spectrophotometer (cf. Charts 2,3).

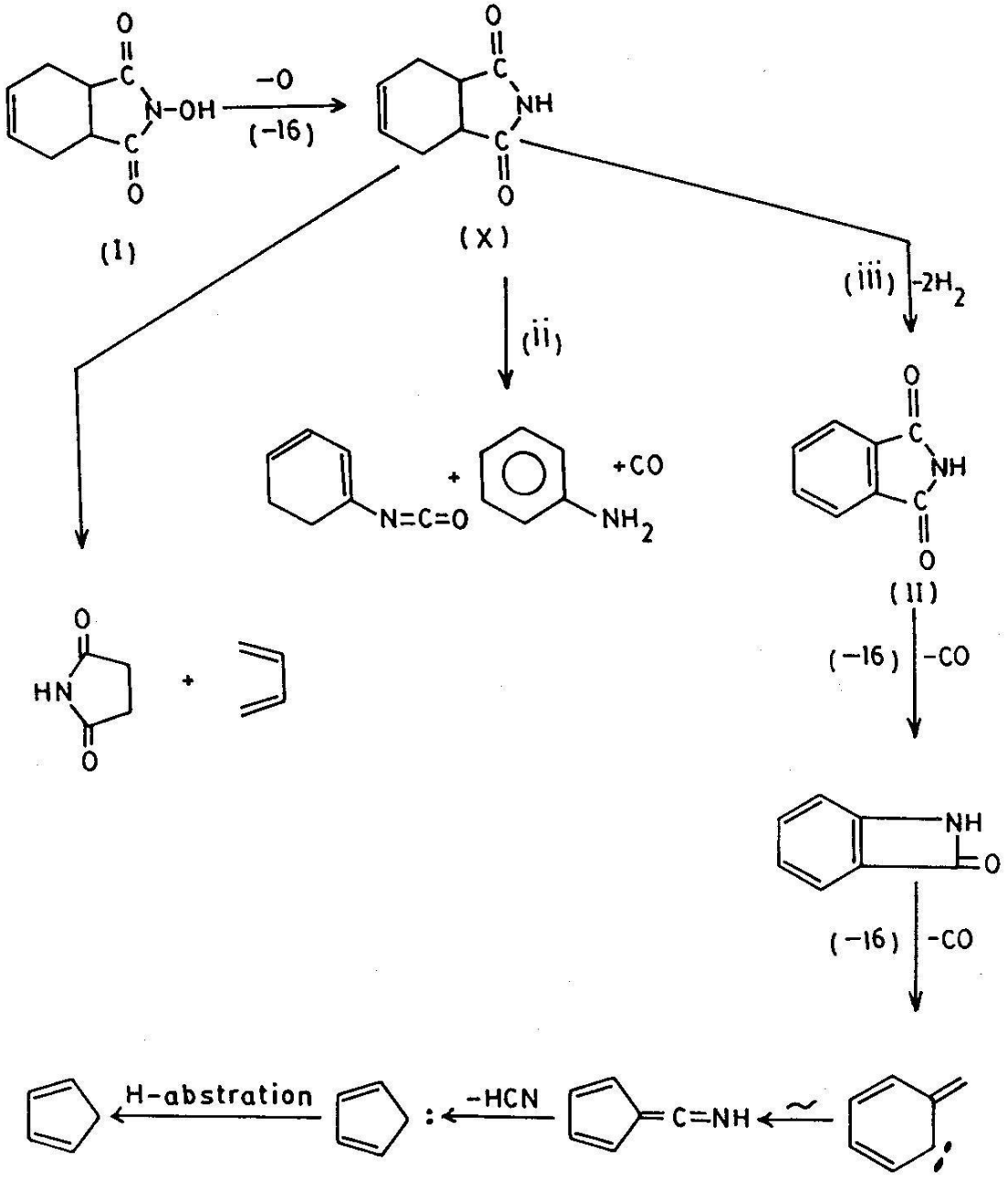
Pyrolysis-mass spectrum of (IVa):

When N-(benzoyloxy)-cyclohex-4-ene-1,2-dicarboximide (IVa) was introduced in the mass spectrometer via a hot indirect inlet system at (300°C), it gives pyrolysis fragmentation pattern via three main routes (cf. Chart 4):

Route (a): Gives cyclohex-4-ene-1,2-dicarboximide (X) (m/z 151), and benzoic acid (m/z 122), which loses CO_2 to give benzene (m/z 78). Cyclohex-4-ene-1,2-dicarboximide undergoes pyrolytic fragmentation via three side routes:

Route (i-a): Involves fragmentation via (retro-Diels-Alder) to give maleimide (m/z 97), and butadiene (m/z 54).

Route (ii-a): Gives cyclohexadiene (m/z 80), benzene (M/Z=78), cyclopentadiene (m/z 66), isocyanate of cyclohex-1,3-diene (m/z 121), aniline (m/z 93) and carbon monoxide.



(Pyrolysis Fragmentation Pattern)

(CHART 1)

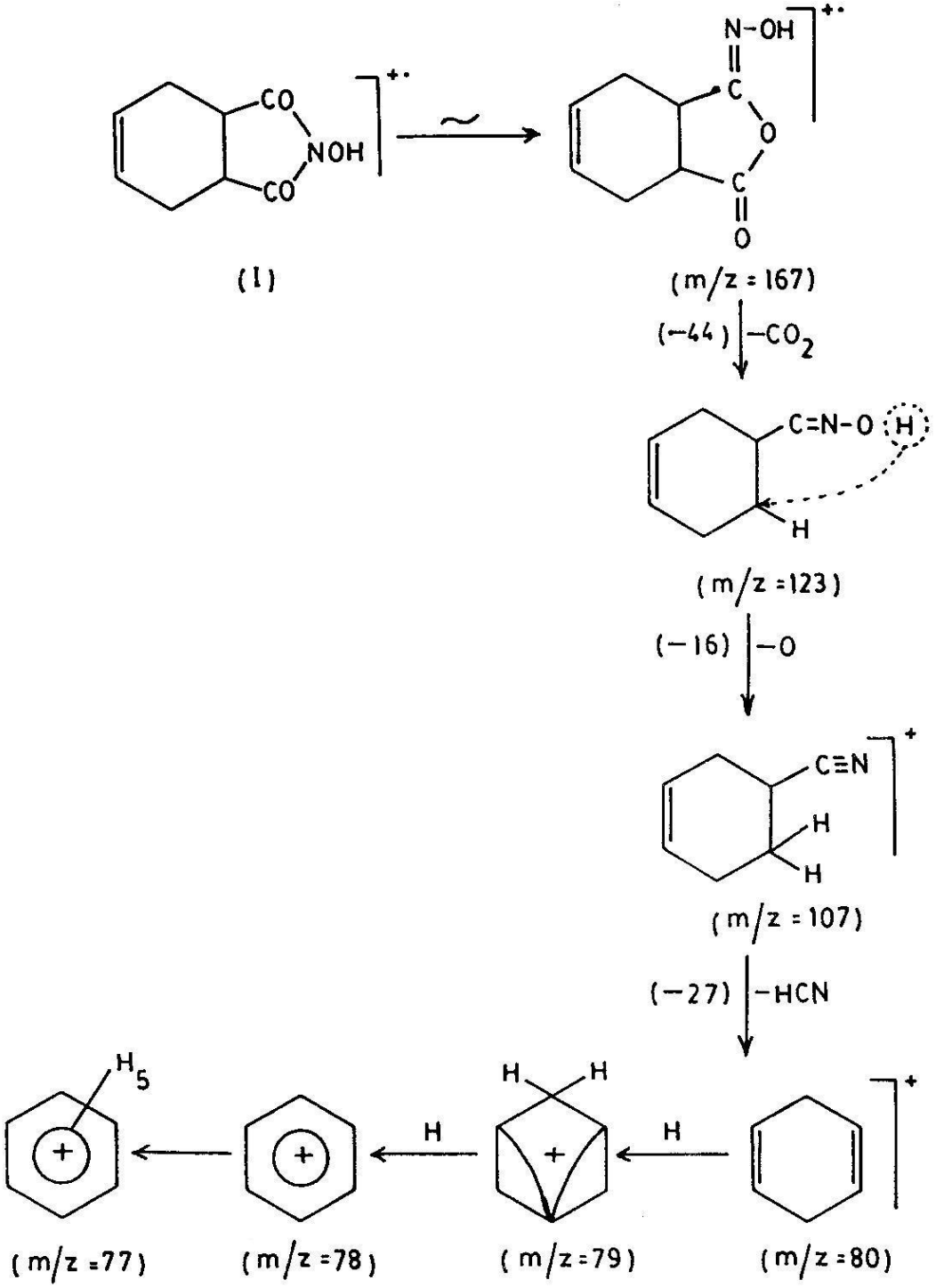
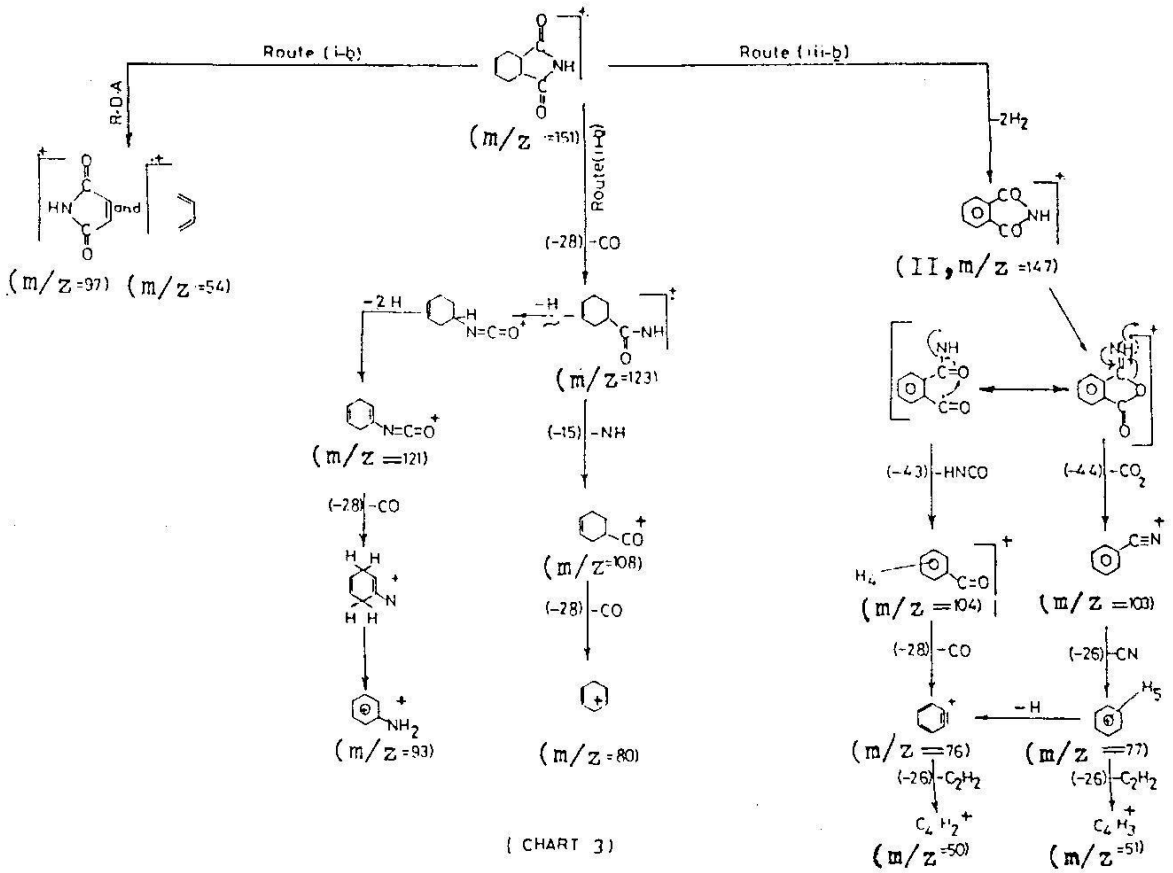

CO
NOH
CO
+·
N-OH
C
O
C
O
(I)
(m/z = 167)
(-44) -CO2
C=N-O
H
H
(m/z =123)
(-16) -O
C≡N
H
H
(m/z = 107)
(-27) -HCN
H5
H
H
H
H
(m/z =77)
(m/z =78)
(m/z =79)
(m/z =80)

CHART = 2



(CHART 3)

Route (iii-a): Gives phthalimide (II) (m/z 147), via aromatization, and benzonitrile (m/z 103).

Route (b): Involves loss of (CO_2) to give N-phenyl-cyclohex-4-ene-1,2-dicarboximide (VIIIa) (m/z 227) which aromatized by loss of hydrogen to give N-phenyl-phthalimide (IXa) (m/z 223).

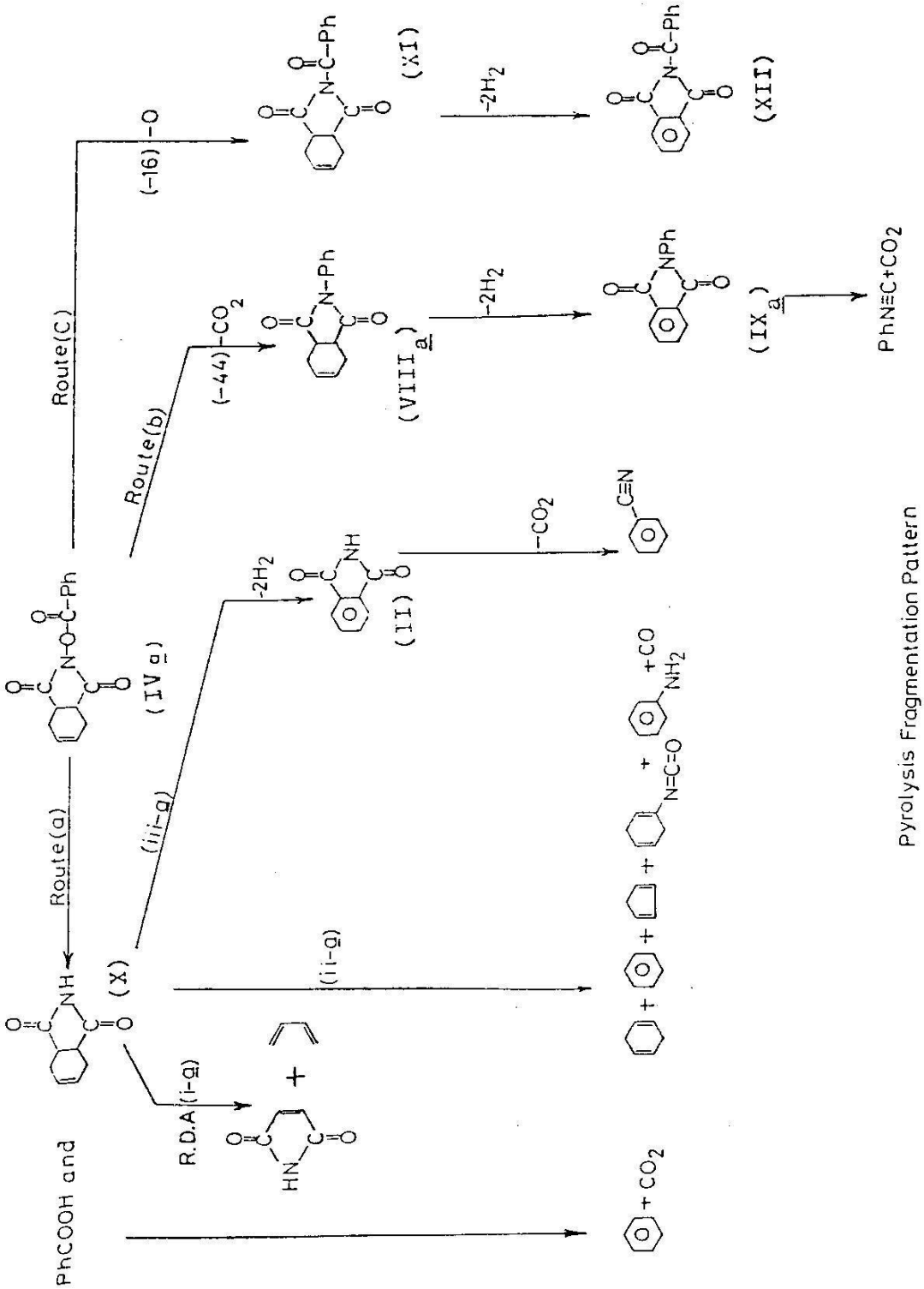
Route (c): Involves loss of oxygen atom to give N-benzoyl-cyclohex-4-ene-1,2-dicaboximide (XI; (m/z 255), which loses hydrogen to give N-benzoyl-phthalimide (XII (m/z 151), via aromatization. This route is similar to pyrolysis of N-hydroxy-phthalimide to phthalimide via loss of oxygen [3].

All the above mentioned compounds showed the expected parent peaks, and mass spectral fragments in the mass spectrophotometer (cf. chart 5).

Pyrolysis-mass spectrum of (VIa):

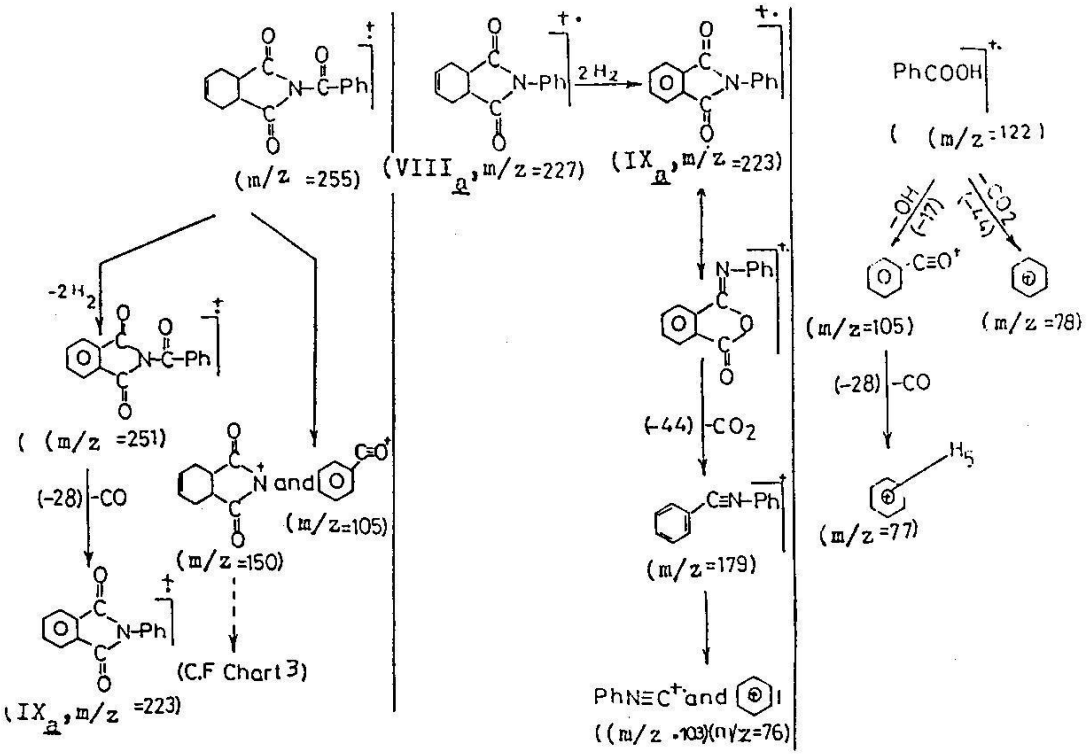
When (VIa) was introduced in the mass spectrometer via a hot indirect inlet system at (280°C), it gives pyrolysis fragmentation pattern via two main routes (cf. chart 6).

Route (a): Involves loss of (SO_2) via rearrangement to give cyclohex-4-ene-1,2-dicarboximide (X) (m/z 251), SO_2, and phenol (m/z 94). Cyclohex-4-ene-1,2-dicarboximide undergoes



Pyrolysis Fragmentation Pattern

(Chart 4)



(CHART 5)

Table-1: m/z values followed by (%) of abundance.

(1)	151(4), 147(2), 123(3), 122(13), 121(12), 108(4), 107(4), 104(25), 103(8), 97(5), 96(2), 93(2), 80(5), 79(65), 78(100), 77(23), 76(29), 66(2), 54(6), 52(12), 51(2), 50(43).
(IVa)	255(2), 251(2), 227(2), 223(2), 179(32), 151(100), 150(32), 147(80), 123(9), 122(40), 121(4), 108(25), 105(96), 104(27), 103(32), 97(2), 96(22), 93(3), 80(42), 79(63), 78(23), 77(92), 76(48), 68(2), 66(19), 54(60), 51(3), 50(36), 43(19).
(VIa)	227(2), 223(2), 179(2), 151(4), 147(16), 123(12), 122(16), 121(11), 108(4), 104(23), 103(26), 97(5), 94(3), 93(3), 80(3), 79(71), 78(100), 77(36), 76(58), 66(31), 54(6), 51(33), 50(29).

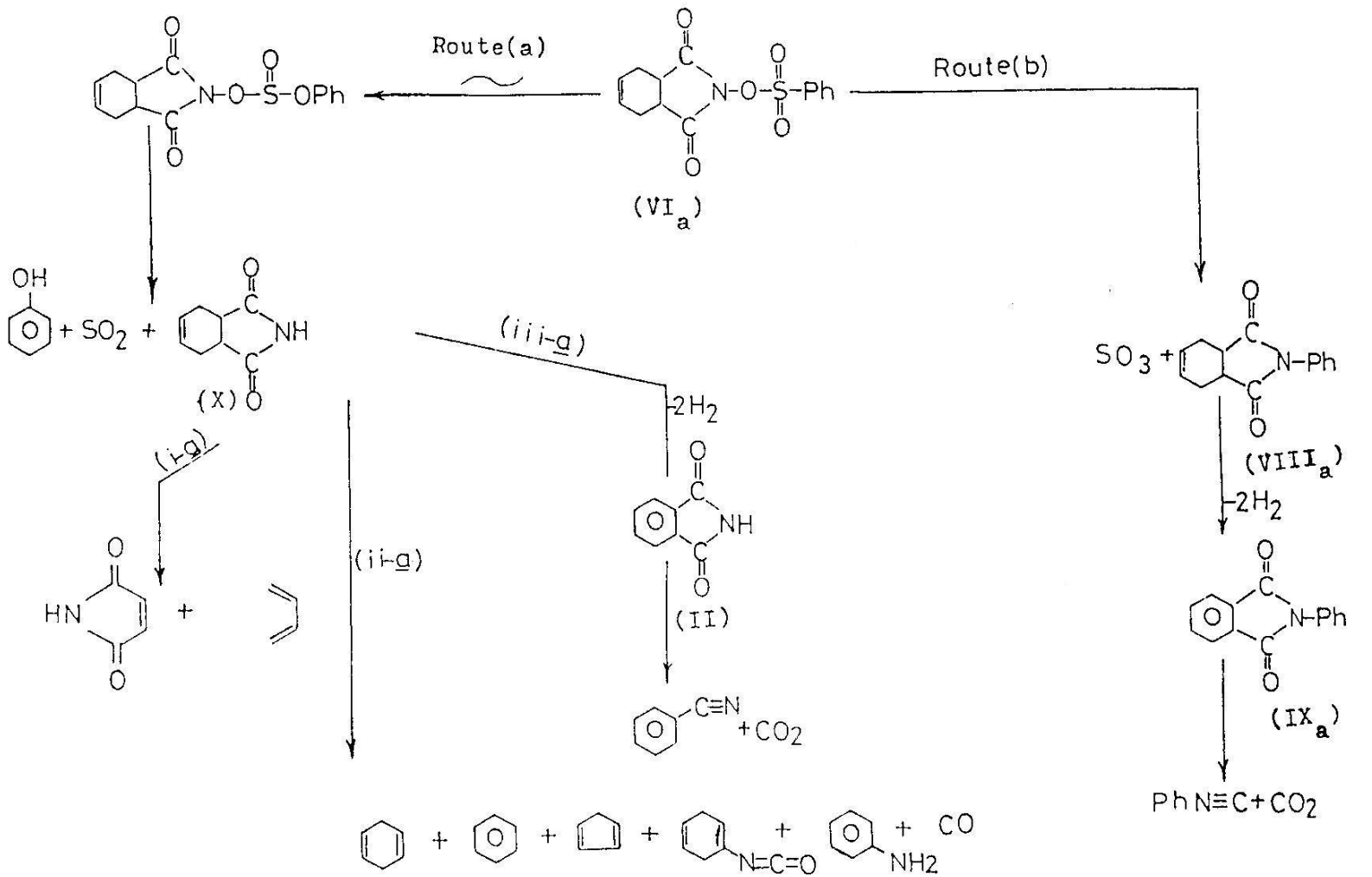


Chart (6) Pyrolysis Fragmentation Pattern

pyrolytic fragmentation via three side routes as in (Chart 6).

Route (i-a): Gives (retro-Diels-Alder) fragmentation products. Maleimide; (m/z 97), and butadiene (m/z 54).

Route (ii-a): Gives cyclohexadiene (m/z 80), benzene (m/z 78), cyclopentadiene (m/z 66), isocyanate of cyclohex-1,3-diene (m/z 121), aniline (m/z 93), and carbon monoxide.

Route (iii-a): Gives phthalimide (II) (m/z 147), benzonitrile (m/z 103), and CO_2.

Route (b): Loss of (SO_3) to give N-phenyl-cyclohex-4-ene-1,2-dicarboximide (VIIIa) (m/z 227), which aromatized to gives N-phenyl-phthalimide (IXa) (m/z 223), the latter gives CO_2 and benzoisonitrile (m/z 103),

All the above mentioned compounds showed the expected parent peaks, and mass spectral fragments in the mass spectrophotometer (cf. Charts 2,5).

Experimental

All melting points are uncorrected, infrared spectra were carried out on a Unicam SP (1200), using Wafer technique, Pyrolysis-mass spectra were determined with varian MAT CH_6 Single Focusing mass spectrometer at a beam energy 70 ev. Samples were introduced via hot indirect inlet system to the source operating temperature at (200°C).

Pyrolysis of N-hydroxy-cyclohex-4-ene-1,2-dicarboximide (I): Formation of phthalimide (II):

N-Hydroxy-cyclohex-4-ene-1,2-dicarboximide (I) was heated at (250°C) on a sand bath for (2 hr). The solid product was obtained in sublimed needles; collected in an air condenser, m.p. 231-232°C (Yield 50%). It was found to be phthalimide from m.p. and mixed m.p. [3] and i.r. spectrum.

Pyrolysis of N-aroyloxy-cyclohex-4-ene-1,2-dicarboximides (IVa-c): Formation of (II) and aromatic acids:

N-Aroyloxy-cyclohex-4-ene-1,2-dicarboximides (IVa-c) were heated at (300°C) on a sand bath for 3 hours. After cooling the solid product obtained was crystallized from ethanol and charcoalized to give (II) (m.p. 230-231°C) [3], (Yield 70%). The mother liquors were concentrated by evaporation to give the corresponding aromatic acids identified by means of m.p. and mixed m.p. [3,4] and i.r. spectra.

Pyrolysis of N-aryl-sulphonyloxy-cyclohex-4-ene-1,2-dicarboximides, (VIa,b): Formation of (II), and aryl-sulphonic acids:

N-Aryl-sulphonyloxy-cyclohex-4-ene-1,2-dicarboximides (VIa,b) were heated at (100°C) on a sand bath for 2 hours. The solid products were recrystallized from ethanol with characoalization to give white crystal, m.p. 230-231°C (Yield 71%). It was proved to be phthalimide from m.p. and mixed m.p. [3] and i.r. spectrum. The mother liquors were evaporated to dryness to give the corresponding aryl-sulphonic acids [3].

Pyrolysis of N-hydroxy-cyclohex-4-ene-1,2-dicarboximide (I): Formation of N-hydroxy-phthalimide (III):

N-Hydroxy-cyclohex-4-ene-1,2-dicarboximide (I) was heated above its m.p. on a sand bath for 1 hour. The solid product was crystallized from ethanol to give solid product m.p.

Table-2

Compound No.	m.p. °C	mixed m.p. °C	Yield %	Ref.
(V a)	163	162	80	[4]
(V b)	152	152	79	[4]
(V c)	165	165	80	[4]

Table-3: Formation of (IXa-d)

Product No.	m.p. °C	Mixed m.p. °C	Yield %	Ref.
(IXa)	204-5	205	38	[4]
(IXb)	201-2	201	39	[4]
(IXc)	155	155	40	[4]
(IXd)	194-5	195	42	[4]

230°C it was proved to be N-hydroxy-phthalimide (III) from m.p. and mixed m.p. [8], and i.r. spectrum.

Pyrolysis of N-aroyloxy-cyclohex-4-ene-1,2-dicarboximides (IVa-c): Formation of N-aroyloxy-phthalimides (Va-c):

The solid (IVa-c) was heated above its m.p. on a sand bath for 1 hour, then cooled. The solid product was crystallized from toluene to give white crystals. It was proved to be N-aroyloxy-phthalimides (V) from m.p. and mixed m.p. [4] and i.r. spectra (cf. Table 2).

Pyrolysis of N-(aryl-sulphonyloxy)-cyclohex-4-ene-1,2-dicarboximides (VIa,b): Formation of N-aryl-sulphonyloxy-phthalimides (VIIa,b):

The solid (VIa,b) was heated above its m.p. on a sand bath for 1 hour then cooled, the solid product recrystallized from ethanol to give white crystals. It was proved to be N-aryl-sulphonyloxy-phthalimides (VIIa,b) from m.p. and mixed m.p. [9], and i.r. spectrum.

Pyrolysis of N-aryl-cyclohex-4-ene-1,2-dicarboximides (VIIIa-d): Formation of N-aryl-phthalimides (IXa-d):

The solid (VIIIa-d) was heated at (380-400°C) on a sand bath for 3 hours. The solid product was treated with alcohol and cooled, then recrystallized from ethanol to give white crystals (IXa-d) (cf. table 3). It was proved to be N-aryl-phthalimides by m.p. and mixed m.p. with authentic sample [4].

References

1. A.F.Fahmy, N.F.Aly, A.Nada and N.Y.Aly, *Bull.Chem.Soc., Japan, 50, 2678 (1977).*

2. A.F.Fahmy, N.F.Aly and M.H. Arief,
Indian J. Chem., **16B**, *697 (1978).*
3. A.F.Fahmy, N.F.Aly and M.O. Orabi,
Bull.Chem.Soc., Japan, **51(7)**, *2148 (1978).*
4. A.F.Fahmy, N.F.Aly and A.H. Abd El-Aleem,
Indian J. Chem., **16B**, *992 (1978).*
5. A.F.Fahmy, N.F.Aly, N.Y.Aly and M.O.Orabi,
Indian J. Chem., **22B**, *912 (1978).*
6. N.F.Aly, M.El-Komy, N.Y.Aly and M.O.Orabi,
Indian J. Chem., **22B**, *471 (1983).*
7. A.F.Fahmy, N.F.Aly, N.Y.Aly and S.A.Essawy,
J.Chem. U.A.R. accepted for publication.
8. B. Lach,
16, *178 (1883).*
9. C.M.Buess and L. Bauer,
J. Org. Chem., **20**, *33 (1955).*