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SPECTROSCOPIC AND STRUCTURAL STUDIES OF SOME OXOCARBON CONDENSATION PRODUCTS—II

A MASS SPECTROMETRIC STUDY OF SOME SUBSTITUTED PHENAZINES AND QUINOXALINES

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Abstract—The mass spectrometric data are reported for 19 condensation products of 5 and 6-membered ring oxocarbons and various *o*-phenylenediamines. The fragmentation mechanisms are discussed and compared with earlier conflicting reports. There is a close similarity between the corresponding 5 and 6-membered ring oxocarbon condensation products in their spectral fragmentation mechanisms which is analogous to the similarity between the fragmentation of the oxocarbons themselves.

INTRODUCTION

A MASS spectrometric study has been carried out on some condensation products, isolated from reactions between *o*-phenylenediamines and monocyclic polycarbonyl compounds, the so called oxocarbons.[1] The characteristic Hinsberg[2] reaction, when applied to the oxocarbons, leads to condensation products which may be considered as derivatives of either phenazine or quinoxaline.

Previously, a low resolution mass spectrometric study of some mono-substituted methyl and methoxy-phenazines, and of some phenazine-N-oxides was reported by Morita.[3] However, more recently, high resolution studies by Holliman *et al.*[4] of a large number of mono- and di-substituted phenazines indicate that some of the earlier reported fragmentation mechanisms must be incorrect. The fragmentation mechanisms observed in this study support the findings of the latter group of workers.

RESULTS AND DISCUSSION

Tetrahydroxy-*p*-benzoquinone dihydrate reacts with *o*-phenylenediamines to give condensation products which have been formulated as 1,2,3,4-tetrahydroxy-phenazines.[5]

The mass spectral data on the 1,2,3,4-tetrahydroxy-phenazines are given in Table 1.

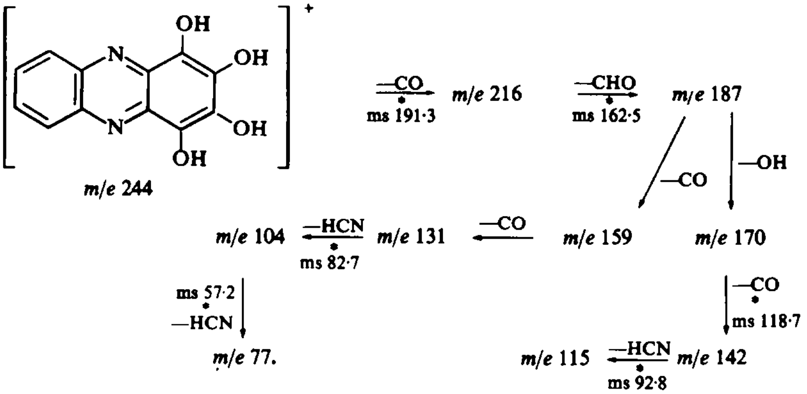
All the tetrahydroxy-phenazine mass spectra show intense parent ion peaks, which are also the base peaks, except in the case of the 7-nitro derivative VI. The fragmentation of compound I may be rationalized on the basis of an initial loss of carbon monoxide followed by the loss of a formyl radical (Diag. 1). The loss of these fragments has been shown to be a characteristic feature of the breakdown of phenols.[6]

The Me derivative (II) spectrum shows prominent P-1 and P-2 peaks at *m*/*e* 257 and *m*/*e* 256, respectively. No intense P-CH_3 (-15) peak is observed. Both the *m*/*e* 257

Table 1. 1,2,3,4-Tetrahydroxy-phenazine mass spectral data

1,2,3,4-Tetrahydroxy-phenazine I	245(17), 244(100), 243(5), 217(6), 216(43), 215(11), 187(15), 170(15), 143(8), 142(29), 132(7), 131(29), 130(11), 129(8), 119(8), 115(12), 114(8), 108(6), 105(6), 104(14), 103(23), 102(20), 92(5), 91(6), 90(6), 88(5), 78(10), 77(33), 76(23), 75(15), 74(6).
7-Methylderivative II	259(16), 258(100), 257(7), 256(13), 230(27), 229(7), 201(6), 184(10), 172(6), 156(14), 155(6), 145(14), 144(23), 143(7), 129(7), 117(11), 116(9), 115(9), 91(10), 90(12), 89(18), 79(7), 78(24), 77(34), 76(14), 75(11).
7,8-Dimethyl-derivative III	273(19), 272(100), 271(9), 270(7), 245(5), 244(32), 243(9), 215(6), 198(10), 170(16), 169(6), 159(17), 158(16), 157(7), 155(5), 136(8), 131(7), 130(5), 116(6), 105(5), 104(7), 103(11), 102(5), 91(7), 79(5), 78(7), 76(14).
7-Chloro-derivative IV	281(5), 280(32), 279(15), 278(100), 252(12), 251(7), 250(36), 249(7), 221(8), 204(11), 192(2), 178(5), 176(13), 165(11), 164(8), 139(6), 138(5), 137(7), 125(6), 114(5), 111(6), 102(8), 100(7), 76(5), 75(9).
7-Carboxyl-derivative V	289(26), 288(100), 272(24), 261(12), 260(77), 259(13), 244(18), 231(21), 214(22), 187(12), 186(45), 175(26), 174(25), 169(12), 147(17), 144(10), 131(15), 130(27), 129(17), 104(14), 103(22), 102(24), 101(10), 93(10), 90(20), 78(12), 77(25), 76(25), 75(29), 74(12).
7-Nitro-derivative VI	290(12), 289(77), 288(60), 287(94), 260(17), 259(92), 258(28), 257(100), 243(25), 231(41), 229(36), 215(32), 204(31), 203(90), 201(20), 187(11), 185(21), 176(46), 175(89), 174(17), 173(60), 157(48), 148(19), 146(13), 145(98), 144(23), 141(11), 130(21), 129(91), 128(41), 118(43), 117(23), 116(14), 103(19), 102(88), 101(70), 100(33), 91(26), 90(34), 89(13), 88(14), 78(28), 77(15), 76(38), 75(95), 74(29).

Note: In general, ions below *m/e* 70 are not shown. Relative abundances of ions are shown in parentheses.



Fragmentations supported by the presence of a metastable peak (ms) are marked with an asterisk.

Diagram 1

and the *m/e* 256 ions are probably stabilized via rearrangement to tropylium-like ions.[4, 6] (Diag. 2)

The fragmentation of the dimethyl compound (III) shows a similar loss of two protons to give probably a tropylium-like ion *m/e* 270. Loss of carbon monoxide is also apparent, resulting in an ion at *m/e* 244 which then loses a methyl-acetylene fragment. Both these eliminations are supported by the appropriate metastable ion peaks at *m/e* 219 and at *m/e* 160·8, respectively.

The spectrum of the chloro compound (IV) shows two ion peaks at *m/e* 280 and

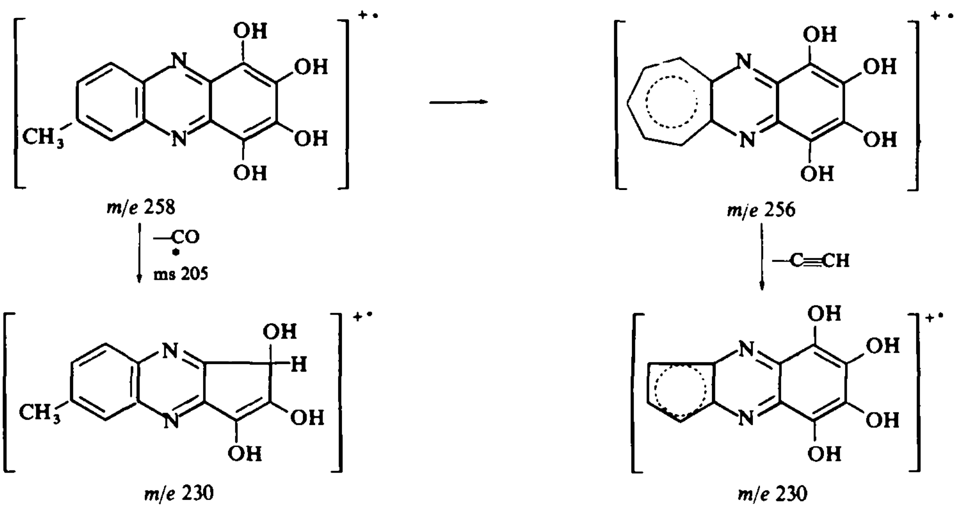


Diagram 2

m/e 278 due to the ^{37}Cl and ^{35}Cl-containing molecular ions. Initial breakdown involves loss of both carbon monoxide and formyl fragments, but not chlorine ions. The presence of the Cl atom appears to stabilize the molecular ion since no P-1 and P-2 ions are observed.

The carboxyl compound (V) gives an extremely complex mass spectrum which features the elimination of not only CO, CHO and HCN fragments, but also the elimination of OH and COOH fragments, as may be expected for a carboxylic acid.[6]

The nitro compound (VI) spectrum is also extremely complex, although the presence of a large number of metastable ion peaks has facilitated its analysis. The parent peak m/e 289 is not the most intense peak, indicating the destabilizing effect of the nitro group. Thus initial fragmentation involves the loss of two protons to give, presumably, the corresponding 7-nitro-2,3-dihydroxy-phenazine-1,4-quinone (XII) ion m/e 287. The loss of the NO_2 fragment occurs to a lesser extent. (Diag. 3)

Rhodizonic acid dihydrate with o-phenylenediamines produces high melting, sparingly soluble solids which have been formulated as 2,3-dihydroxy-1,4-dihydro-1,4-dioxo-phenazines (2,3-dihydroxy-phenazine-1,4-quinones).[5]

Their mass spectral data are given in Table 2.

It is of interest to note that these phenazine-quinone spectra all show two intense peaks due to the molecular ion (M) and M-4CO ions. The latter are probably due to the stable quinoxaline ions.

The 2,3-dihydroxy-phenazine-1,4-quinone (VII) breakdown may be represented as follows: (Diag. 4).

In the fragmentation of the Me compound (VIII) loss of protons from the Me group and rearrangement to tropylium-like ions does not appear to be energetically favourable until all the carbon monoxide fragments are eliminated, and then the methyl group rearrangement competes with HCN elimination (Diag. 5).

A similar breakdown scheme appears to operate in the case of the dimethyl derivative (IX).

The chloro compound (X) fragmentation is similar to that of the other phenazine-

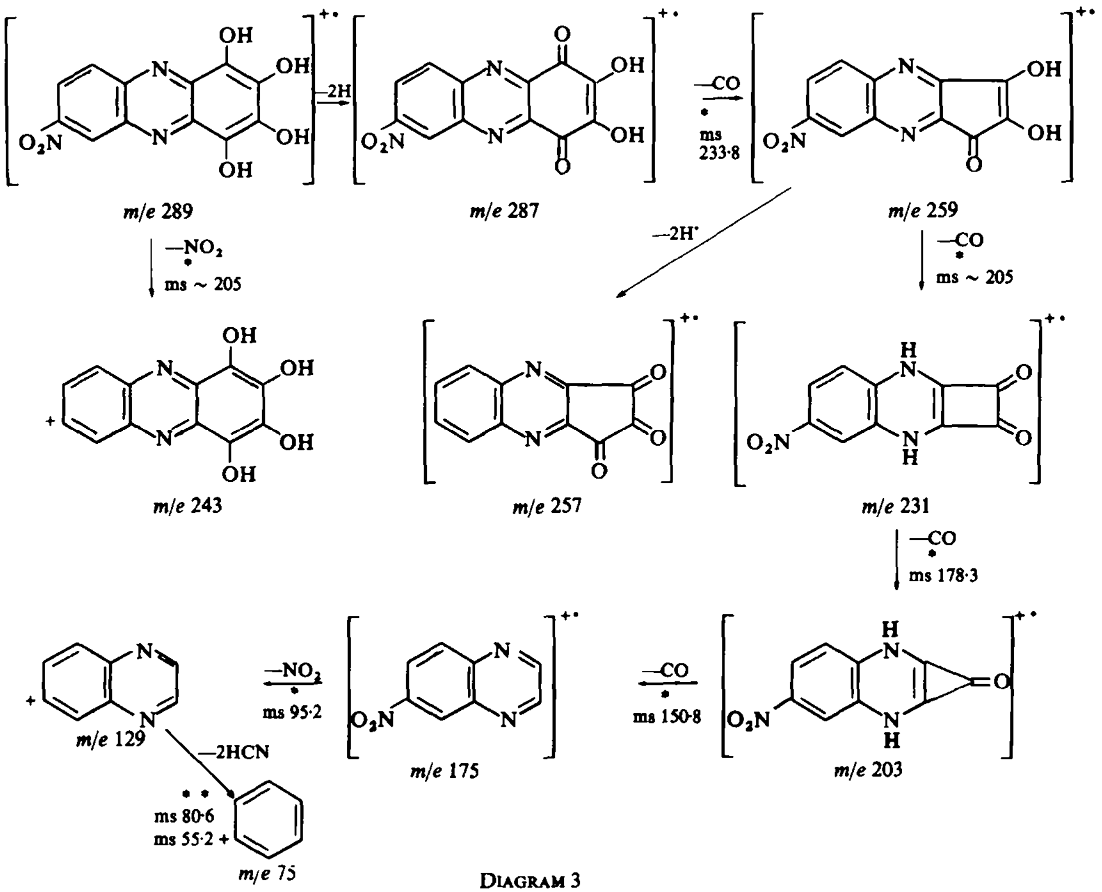


Diagram 3

Table 2. 2,3-Dihydroxy-phenazine-1,4-quinone mass spectral data

2,3-Dihydroxy-phenazine-1,4-quinone VII	244(12), 243(20), 242(90), 215(6), 214(33), 186(12), 170(13), 159(8), 158(77), 142(10), 131(20), 130(100), 129(30). 128(5), 114(5), 104(11), 103(92), 102(68). 101(12), 90(5). 88(5), 78(7), 77(9). 76(6), 75(44),74(8).
7-Methyl derivative VIII	258(8), 257(17), 256(100), 228(19), 200(11), 184(8), 173(5), 172(44), 156(5), 145(13), 144(99), 143(17), 117(24), 116(19), 115(6), 114(6), 100(7), 91(5), 90(31), 89(44), 88(7), 77(7), 76(5), 72(8).
7,8-Dimethyl derivative IX	272(11), 271(11), 270(61), 242(16), 214(9), 198(8), 186(27), 159(13), 158(100), 157(16), 131(27), 130(10), 128(5), 116(11), 104(17), 103(24), 102(9), 101(5), 91(5), 89(6), 79(7), 78(13), 77(26), 76(6), 75(5).
7-Chloro derivative X	278(20), 277(9), 276(52), 250(7), 248(17), 220(9), 204(6), 194(16), 193(6), 192(46), 176(5), 166(32), 165(6), 164(100), 163(16), 139(19), 138(11), 137(52), 136(21), 127(8), 112(7), 111(5), 110(21), 109(5), 102(19), 101(10). 100(40), 99(5), 85(5), 82(6), 78(5), 76(15), 75(29), 74(17).
7-Carboxyl derivative XI	288(7), 287(5), 286(28), 258(8), 230(3), 214(3), 202(19), 186(3), 175(46), 173(5), 147(2), 130(4), 129(4), 127(4), 120(3), 118(5), 103(4), 102(7), 101(5), 100(5), 90(8), 78(3), 76(7), 75(11), 74(4), 18(100).
7-Nitro derivative XII	288(7), 287(46), 259(15), 231(4), 203(33), 176(6), 175(60), 157(7), 148(3), 145(5), 129(24), 128(8), 102(31), 101(15), 100(7), 90(5), 78(8), 76(9), 75(25), 74(8), 18(100).

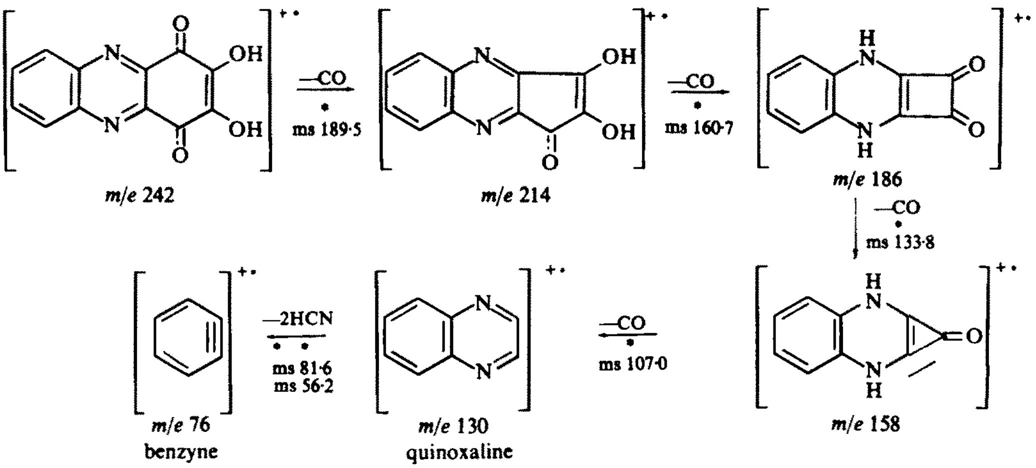


DIAGRAM 4

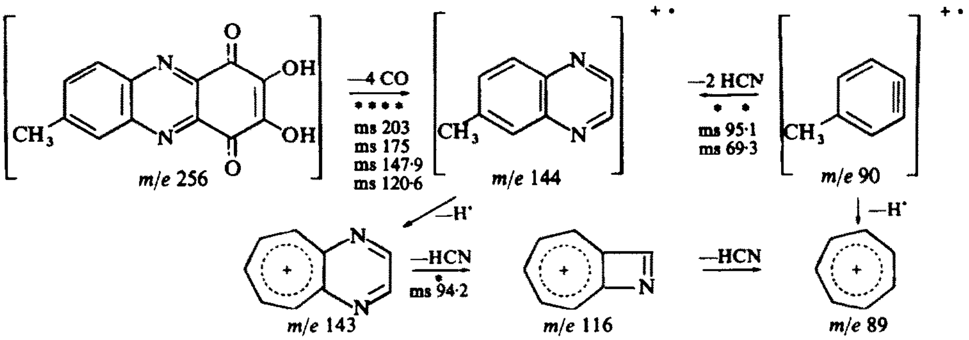


DIAGRAM 5

quinones. Chlorine elimination becomes important only after the loss of four CO and one HCN fragments has taken place.

The carboxyl compound (XI) also shows this characteristic elimination of four CO fragments. Further breakdown is via the loss of HCN, COOH and HCN fragments to yield the benzyne ion.

The nitro compound (XIII) appears to break down to the nitro-quinoxaline ion. Further fragmentation favours the elimination of the nitro group rather than hydrogen cyanide, although both are observed.

The ion *m/e* 145 could arise from the elimination of NO to yield a quinoxaline-phenozy cation. (Diag. 6).

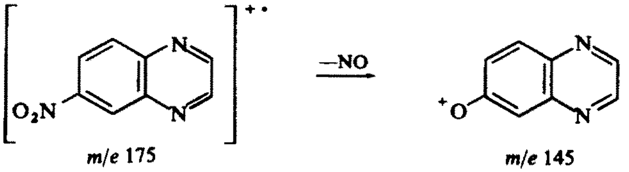


DIAGRAM 6

This unusual rearrangement has been observed in the mass spectral fragmentation of nitrobenzene.[7]

The tetrahydroxy-phenazines and the phenazine-quinones can be readily oxidized to hydrated yellow compounds, which can also be obtained from triquinoyl octahydrate and *o*-phenylenediamines. These compounds have been postulated as phenazine-1,2,3,4-tetrones.[8] However, the role of the water molecules in the molecular structures has not been clarified.[5]

The mass spectral data of these 1,2,3,4-tetrahydro-1,2,3,4-tetra-oxo-phenazines (phenazine-1,2,3,4-tetrones) are given in Table 3.

Table 3. Phenazine-1,2,3,4-tetrone mass spectral data

Phenazine-1,2,3,4-tetrone XIII	242(6), 214(2), 186(1), 184(6), 174(5), 158(5), 157(3), 156(25), 131(2), 130(22), 129(11), 128(48), 103(14), 102(11), 101(13), 100(2), 88(2), 78(3), 77(4), 76(17), 75(12), 74(4), 44(100), 18(90).
7-Methyl derivative XIV	256(18), 228(10), 200(6), 198(9), 184(8), 172(23), 171(9), 170(37), 156(8), 145(13), 144(100), 143(24), 142(63), 141(22), 117(45), 116(30), 115(36), 114(26), 90(31), 89(45), 88(15), 78(9), 77(9), 76(10), 75(9)
7,8-Dimethyl derivative XV	270(15), 242(5), 214(2), 186(7), 184(9), 159(3), 158(27), 157(6), 156(12), 155(3), 141(9), 131(8), 130(3), 128(3), 116(4), 114(4), 104(5), 103(7), 102(4), 89(3), 78(4), 77(8), 76(3), 44(100), 18(82).
7-Carboxyl derivative XVI	286(16), 258(19), 244(5), 230(3), 228(11), 203(3), 202(21), 201(9), 200(71), 175(6), 174(49), 173(14), 172(79), 157(3), 156(6), 155(47), 147(17), 129(4), 128(7), 127(36), 120(5), 118(5), 103(5), 102(8), 101(11), 100(18), 90(9), 87(4), 76(12), 75(21), 74(9), 44(100).

The mass spectra all show a parent ion peak corresponding to *m*/*e* M + 2 (M = mass of anhydrous tetrone). The two protons may be attached to either the two nitrogen atoms or to two oxygen atoms. (Diag. 7).

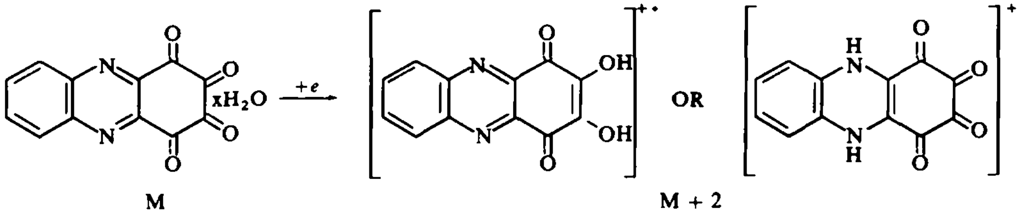


Diagram 7

It is possible that some of the CO groups are hydrated to the *gem*-diol form which could then lose two hydroxyl groups to give structure (a) and possibly (b) as well, by proton migration. (Diag. 8).

The phenazine-tetrones, apart from the Me-compound (XIV), give the base peak at *m*/*e* 44 which is probably the carbon dioxide ion peak. It is possible that both electron impact as well as thermal fragmentation is taking place. Eistert *et al.*[8] have proposed a so-called thermal "redox-disproportionation" of phenazine-1,2,3,4-tetrone dihydrate (XIII) in which carbon dioxide is given off. The phenazine-tetrone

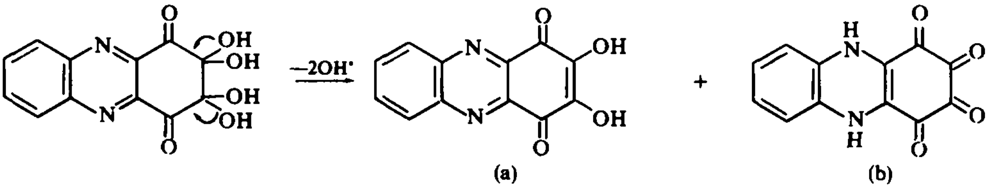


DIAGRAM 8

fragmentation can be illustrated by the breakdown pattern given by phenazine-1,2,3,4-tetrone (XIII). (Diag. 9).

The 5-membered ring oxocarbon croconic acid gives similar mono-condensation products with *o*-phenylenediamines. These products have been formulated as quinoxalino [2.3-d] cyclopentadienones.[5]

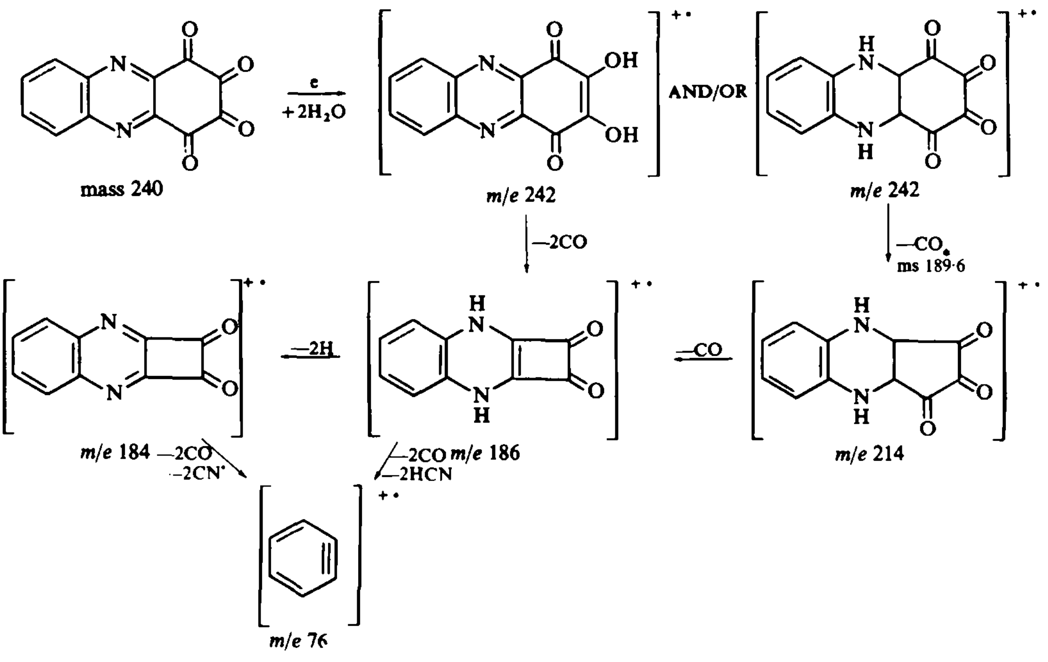


DIAGRAM 9

Oxidation of compound XVIII yields a quinoxalino-[2.3-d]-cyclopentane-1,2,3-trione (XX), which may be considered as a mono-condensation product of the oxocarbon leuconic acid pentahydrate.[5]

Their mass spectral data are given in Table 4.

The mass spectral fragmentation of these condensation products is very similar to the corresponding six-membered ring oxocarbon condensation products. This is hardly surprising since these molecular ions are all observed as fragment ions in the mass spectra of the 6-membered ring precursor compounds.

The close similarily of the mass spectral fragmentation of the oxocarbons has been reported earlier[9] and this study clearly illustrates also the close similarity between the oxocarbon condensation products.

Table 4. Croconic acid condensation product mass spectral data

Quinoxalino-[2.3-*d*]-2,3-dihydroxy-Cyclopentadien-1-one XVIII	215(12), 214(78), 186(6), 159(6), 158(53), 131(23), 130(99), 129(37), 128(10), 114(5), 104(15), 102(83), 101(16), 100(6), 90(6), 88(7), 78(9), 77(17), 76(100), 75(62), 74(18).
6,7-Dimethylquinoxalino-[2.3-*d*]-2,3-dihydroxycyclopentadien-1-one XIX	243(7), 242(48), 214(4), 171(2), 159(8), 158(66), 157(10), 143(2) 131(17), 130(6), 116(5), 104(9), 103(13), 102(5), 78(6), 77(11), 18(100).
Quinoxalino-[2.3-*d*]-cyclopentane-1,2,3-trione XX	212(3), 185(3), 184(25), 157(6), 156(41), 129(10), 128(100), 102(5), 101(24), 100(3), 78(7), 77(5), 76(13), 75(14), 74(6).

EXPERIMENTAL

The mass spectra were measured on an A.E.I. MS.12 mass spectrometer. The standard Bleakney type source was used and the compounds were inserted via the direct insertion probes, with source temperatures in the range 150°–330°.

The electron beam energy was at 70 eV, run from a rhenium filament, with the ionizing current at 100 μA.

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