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SPECTROSCOPIC AND STRUCTURAL STUDIES OF SOME OXOCARBON CONDENSATION PRODUCTS—III

A SPECTROSCOPIC AND MASS SPECTRAL INVESTIGATION OF SOME CYCLOBUTA-[b]-QUINOXALINES[1]

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Abstract—IR and H-NMR and mass spectral data are reported for the condensation products formed between squaric acid and some *o*-phenylenediamines. The data are interpreted in favour of the condensation products being formulated as 1,2,3,8-tetrahydro-1,2-dioxo-cyclobuta[b]quinoxalines.

INTRODUCTION

IN A previous communication[2] the synthesis and preliminary characterization of a new series of heterocyclic compounds, the cyclobuta [*b*] quinoxalines, was reported. The results of further spectroscopic and mass spectrometric studies on these compounds are now reported and discussed.

RESULTS AND DISCUSSION

The characteristic Hinsberg[3] reaction given by α-diketones with *o*-phenylenediamines has been previously studied with a number of cyclobutenediones. Both phenyl-cyclobutene-dione[4] and diphenyl-cyclobutene-dione[5] reacted with *o*-phenylenediamine, but did not yield the expected cyclobutadieno-quinoxalines. In both cases rupture of the cyclobutene-dione ring occurred to give substituted quinoxalines. More recently, high melting, coloured 1-phenyl-cyclobuta [*b*] quinoxaline-[8*H*]-2-ones have been obtained from reactions between 1-bromo-2-phenyl-1-cyclobutene-3,4-dione and *o*-phenylenediamines.[6]

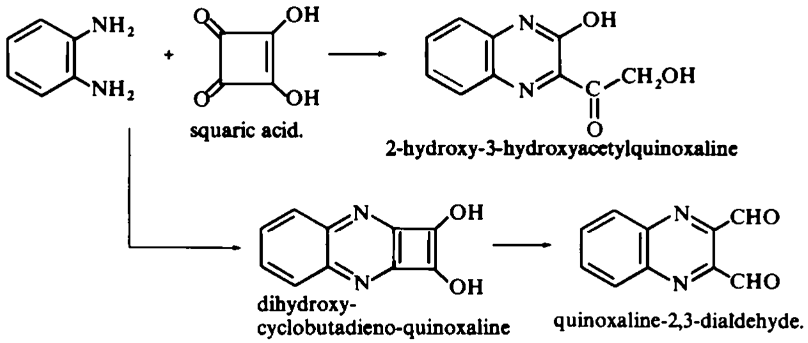
The reaction between 3,4-dihydroxy-cyclobut-3-ene-1,2-dione (squaric acid) and *o*-phenylenediamines also yields high melting coloured compounds.[2] If the reaction should proceed in the same way as that between the phenyl-cyclobutene-diones[4, 5] and *o*-phenylenediamines, then squaric acid should yield 2-hydroxy-3-hydroxyacetylquinoxaline rather than dihydroxy-cyclobutadieno-quinoxaline. It is possible that in the latter compound rupture of the cyclobutadiene ring could occur to give quinoxaline-2,3-dialdehyde. (Diag. I.)

It is also possible that the reaction could proceed in the same way as that between 1-bromo-2-phenyl-1-cyclobutene-3,4-dione and *o*-phenylenediamine,[6] although in this case both mono- and di-condensation products should result. (Diag. II.)

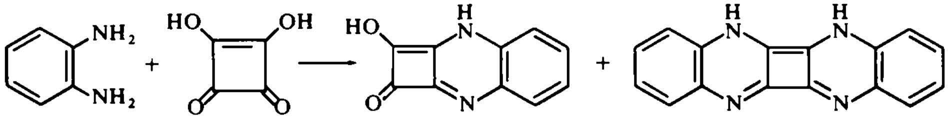
Another possibility is that the reaction products might be analogous to the betaine-type molecules isolated from reaction between squaric acid and both primary and secondary amines.[7] (Diag. III.)

However elemental analyses indicate that mono-condensation products result. IR and proton NMR studies clearly suggest that these reaction products may be formulated as 1,2,3,8-tetrahydro-1,2-dioxocyclobuta [*b*] quinoxalines. (Diag. IV.)

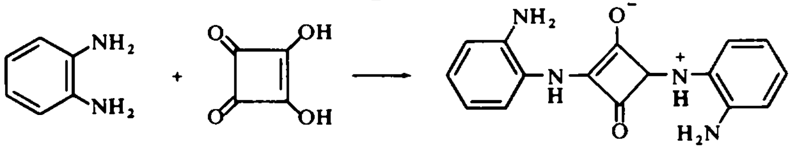
DIAG. I



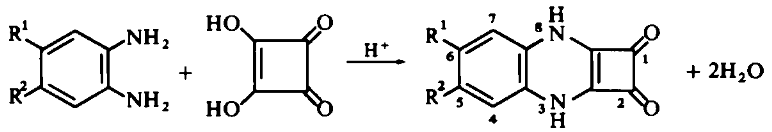
DIAG. II



DIAG. III



DIAG. IV



(A) $R^1 = R^2 = H$
(B) $R^1 = H, R^2 = CH_3$
(C) $R^1 = R^2, CH_3$

(D) $R^1 = H, R^2 = Cl$
(E) $R^1 = H, R^2 = COOH$, (monohydrate)
(F) $R^1 = H, R^2 = NO_2$, (monohydrate)

Their IR spectra show strong to medium intensity bands in the region 3200 cm^{-1} to 2,500 cm^{-1} (Table 1). These bands may be assigned to H-bonded N—H stretching vibrations. The bands observed at higher frequencies in the spectra of compounds (C), (E) and (F) are probably due to ν_{O-H} vibrations. The analytical data suggest that these three compounds are hydrated. The strong bands in the region 1,818 cm^{-1} to 1,795 cm^{-1} can be assigned to $\nu_{C=O}$ vibrations; bands in this region being characteristic of the cyclobutene-dione structure.[4, 8, 9] The presence of these bands rules out all the alternative structures suggested in Diags I, II and III. Furthermore, the quinoxaline-2,3-dialdehyde has been isolated[10] and shown to have a strong sharp $\nu_{C=O}$ band at 1,721 cm^{-1} [11]

Table 1. IR Spectral data for some cyclobuta[*b*]quinoxalines in the region 3,600 cm^{-1} to 1,300 cm^{-1}

Compound											
(*A*)		(*B*)		(*C*)		(*D*)		(*E*)		(*F*)	
				3540 cm^{-1}	W					3590 cm^{-1}	S
				3440 cm	W			3400 cm^{-1}	S	3510	S
3180 cm^{-1}	S	3180 cm^{-1}	S	3180	S	3175 cm^{-1}	S	3200	VS	3170	M
3130	S	3135	S	3120	S	3120	S	3050	S	3115	S
2960	S	2955	S	2930	S	2980	S	2990	S	3040	M
2885	S	2880	S	2865	S	2950	S	2730	M	2920	S
2790	S	2810	S	2765	S	2860	S	2540	M	2850	S
1818	S			1808	S			1812	VS		
1800	S	1800	S	1795	M	1805	S	1802	VS	1800	S
1655	VS	1670	VS	1640	VS	1675	VS	1695	VS	1700	S
1610	VS	1620	VS	1570	VS	1625	VS	1640	VS	1630	S
1560	VS	1585	VS	1550	VS	1580	VS	1590	VS	1590	S
1495	VS	1550	S	1465	S	1545	VS	1575	VS	1490	S
1470	VS	1500	VS	1410	VS	1490	VS	1535	S	1425	M
1370	VS	1460	S	1385	S	1415	S	1490	S	1330	S
1315	VS	1420	S	1350	S	1350	S	1420	S		
		1360	S					1330	S		

VS = very strong; S = strong; M = medium; W = weak.

Table 2. H-NMR data for some cyclobuta[*b*]quinoxalines[a]

Compound	Aromatic ring protons[b,c]					N-H Protons[b]	CH$_3$ Protons[b]	OH Protons[b]
	τ_A	τ_B	τ_X	J_{AB}	J_{BX}			
(A)	3·26	−3·74	multiplet			0·04	—	—
(B)	3·73	3·54	3·81	∼7·2	—	0·07	7·98 (Py)	—
(C)		3·84 singlet				0·07	8·04 (Py)	5·66 4·93 (Py)
(D)	3·70	3·33	3·70	∼8·4	∼2·4	−0·07	—	—
(E)	3·64	2·81	3·165	∼8·4	∼1·8	−0·13, −0·26	—	4·80 4·52 (Py)
(F)	3·64	2·47	3·04	∼8·4	∼2·4	−0·31, −0·55	—	—

[a] All spectra were taken on dimethyl sulphoxide solutions apart from those studied in pyridine (Py).

[b] All chemical shifts are reported on the τ scale.

[c] All coupling constants are in Hz.

The intense bands in the region 1,700 cm^{-1} to 1,610 cm^{-1} may be due to the cyclobutene ring C=C stretching vibrations. Analogous C=C stretching bands have been observed in non-conjugated alkenes between 1,680 cm^{-1} and 1,620 cm^{-1},[12] hence it is possible that the cyclobuta [*b*] quinoxalines do not have completely planar, fully conjugated structures.

The ring proton NMR spectrum of the unsubstituted compound (A) shows a typical A_2B_2 multiplet centred at $\tau = 3{\cdot}50$ ppm, in contrast to the quinoxaline-2,3-

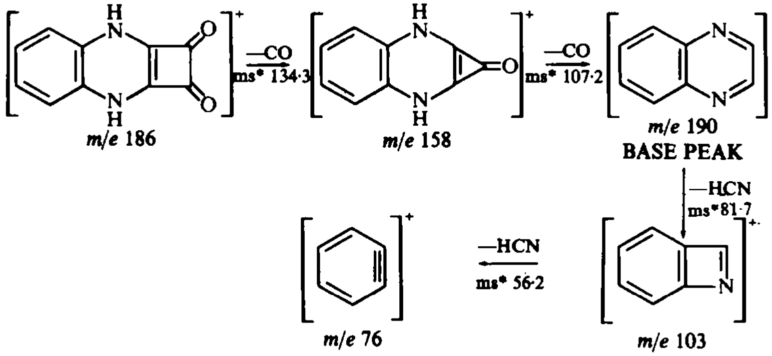
dialdehyde multiplet at $\tau = 2{\cdot}00$ ppm[11] (Table 2). Furthermore, the quinoxaline-2,3-dialdehyde also gives a sharp aldehydic proton signal at $\tau = -0{\cdot}28$ ppm, whereas all of these condensation products show quadrupole broadened low-field signals.

The dimethyl compound (C) has the expected single ring proton signal. The ring proton spectra of the other compounds are analysed on the basis of an AB type of spin system.

The chloro (D), carboxyl (E) and nitro (F) substituent groups produce an increasingly greater deshielding of the N—H protons and in the latter two compounds the shielding at each of the two N—H proton sites is sufficiently different to give rise to a low field doublet.

As indicated previously,[2] the mass spectral fragmentation of these cyclobuta [*b*] quinoxalines involves the successive loss of two carbon monoxide fragments, followed by a further loss of two hydrogen cyanide fragments. The fragmentation may be illustrated by the breakdown pattern for compound (A) (Diag. V).

Diag. V

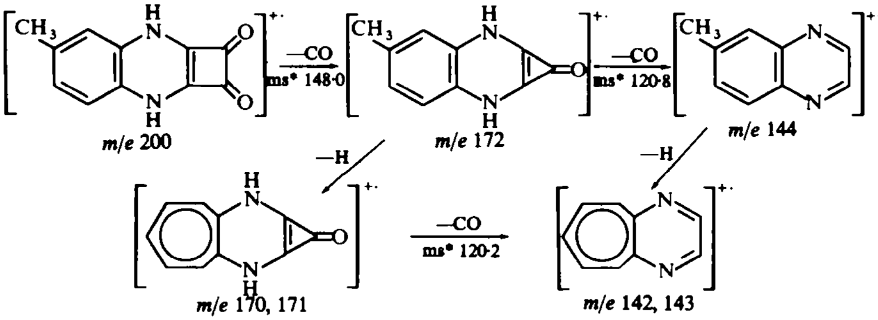


Steps characterized by the appropriate metastable peaks are given as ms.*

The major ion peaks, and relative abundances observed in the mass spectra of all the condensation products are given in Table 3.

The mono-(B) and di-methyl (C) compounds follow very similar fragmentation paths. The presence of, for example in compound (B), prominent peaks at *m/e* 171, 170, 143 and 142 suggests that loss of protons from the methyl group is taking place, with stabilization of the products via rearrangement to tropylium-like ions (Diag. VI).

Diag. VI



The proposed structure for *m/e* 143 is supported by an accurate mass measurement, which gives a value of 143·0604. $C_9H_7N_2$ requires 143·06915.

TABLE 3. MASS SPECTRAL DATA FOR SOME CYCLOBUTA[*b*]QUINOXALINES

Compound	
(A)	186^+ (44), 159^+ (10), 158^+ (72), 131^+ (10), $\underline{130^+ (100)}$, 129^+ (18), 103^+ (74), 102^+ (26), 76^+ (44), 75^+ (20), 18^+ (44).
(B)	200^+ (30), 173^+ (9), 172^+ (65), 171^+ (9), 170^+ (19), 144^+ (58), 143^+ (13), 142^+ (15), 117^+ (6), 116^+ (3), 115^+ (4), 90^+ (4), 89^+ (5), 28^+ (8), $\underline{18^+ (100)}$, 17^+ (27).
(C)	214^+(4), 186^+ (6), 185^+ (2), 184^+(5), 158^+ (13), 157^+ (4), 156^+ (6), 141^+ (7), 131^+ (6), 104^+ (3), 103^+ (4), 77^+ (4), 28^+ (24), $\underline{18^+ (100)}$, 17^+ (61).
(D)	222^+ (16), 221^+ (5), 220^+ (36), 194^+ (4), 192^+ (11), 166^+ (2), 164^+ (6), 139^+ (4), 137^+ (11), 110^+ (6), 102^+ (9), 100^+ (27), 74^+ (4), 28^+ (42), $\underline{18^+ (100)}$, 17^+ (80).
(E)	230^+ (22), 202^+ (42), 188^+ (22), 175^+ (11), $\underline{174^+ (100)}$, 173^+ (13), 161^+ (22), 147^+ (41), 129^+ (11), 128^+ (20), 127^+ (12), 120^+ (16), 188^+ (13), 103^+ (16), 102^+ (18), 101^+ (12), 90^+ (16), 76^+ (16), 75^+ (30), 44^+ (66), 28^+ (39), 18^+ (20).
(F)	231^+ (26), 203^+ (47), 201^+ (7), 176^+ (10), $\underline{175^+ (100)}$, 173^+ (13), 157^+ (12), 148^+ (6), 143^+ (8), 130^+ (8), 129^+ (35), 128^+ (14), 102^+ (80), 101^+ (28), 100^+ (19), 78^+ (13), 76^+ (22), 75^+ (59), 74^+ (29), 63^+ (23), 52^+ (23), 51^+ (24), 50^+ (31).

In the chloro compound (D) loss of Cl does not appear to be energetically favourable until 2 CO and one HCN fragment have been eliminated.

The fragmentation of the nitro compound (F) is more complex. The initial loss of a CO fragment is followed by the loss of both CO and NO_2 and further fragmentation shows elimination of both NO_2 and HCN fragments. This behaviour has been observed previously in a similar condensation product obtained from the oxocarbon, rhodizonic acid.[1]

The electronic spectra of all these compounds show a large number of absorption bands and distinct shoulders.[13] The interpretation of these will be attempted when a more complete picture of the electronic structure of these compounds is available. The close similarity of the electronic spectra of compound (A) and benzo-cyclobutadienoquinone[14] provides further support for the proposed structures of these condensation products.

The spectroscopic and mass spectral data clearly support the proposed structures for these condensation products.

EXPERIMENTAL

The preparative methods have been described previously.[2]

Compound (*A*)—red solid, m.p. ~330° dec. (Found: C, 64·41; H, 3·35; N, 14·96. Calc. for $C_{10}H_6N_2O_2$: C, 64·51; H, 3·25; N, 15·05%).

Compound (*B*)—brown solid, m.p. ~280–290° dec. (Found: C, 65·80; H, 4·01; N, 13·88. Calc. for $C_{11}H_8N_2O_2$: C, 65·99: H, 4·03; N, 13·99%).

Compound (*C*)—orange solid, m.p. ~285–295° dec. Found: C, 66·82; H, 4·79; N, 12·89%. Calc. for $C_{12}H_{10}N_2O_2$: C, 67·28; H, 4·71; N, 13·08%).

Compound (*D*)—brown crystals, m.p. 305–310° dec. (Found: C, 54·38; H, 2·61; N, 12·73. Calc. for $C_{10}H_5N_2O_2Cl$: C, 54·44; H, 2·28; N, 12·70%).

Compound (*E*)—yellow solid, m.p. >310°. (Found: C, 52·99; H, 3·45; N, 11·45. Calc. for $C_{11}H_6N_2O_4 . H_2O$: C, 53·23; H, 3·25; N, 11·29%).

Compound (*F*)—red-brown solid, m.p. ~290–295° dec. (Found: C, 48·96; H, 2·93; N, 16·77. Calc. for $C_{10}H_5N_3O_4 . H_2O$: C, 48·20; H, 2·83; N, 16·87%).

IR spectra were measured on a Perkin–Elmer 337E grating spectrophotometer. All samples were prepared as nujol and hexachlorobutadiene mulls.

The ^{1}H-NMR spectra were measured on a Perkin–Elmer R10 (60 MHz) instrument. TMS was used as an internal reference in all measurements.

The mass spectra were obtained with an AEI MS12 mass spectrometer. An electron beam energy of 70 eV, with an ionizing current of 100 μA, was used in all measurements. The samples were introduced via the direct insertion probes.

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