# Synthesis of Cyclobuta[*b*]quinoxalines

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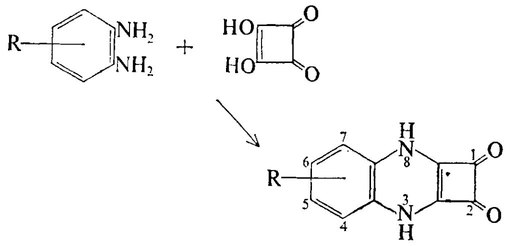
THE characteristic condensation reaction between α-diketones and *o*-phenylenediamines has now been investigated with a number of cyclobutenediones. Phenylcyclobutadienoquinone reacted with *o*-phenylenediamine to give 2-phenylacetylquinoxaline.[1] Similarly, diphenylcyclobutadienoquinone gave 2-phenyl-3-phenylacetylquinoxaline.[2] In both examples cleavage of the four-membered ring occurred to yield substituted quinoxalines and not the expected condensed cyclobutadienoquinoxalines. Recently, the preparation of 1-phenylcyclobuta[*b*]quinoxalin-8*H*-2-ones from *o*-phenylenediamines and 1-bromo-2-phenylcyclobut-1-ene-3,4-dione has been reported.[3]



We now report a new preparation of condensed cyclobuta[*b*]quinoxalines from *o*-phenylenediamines and 3,4-dihydroxycyclobut-3-ene-1,2-dione (squaric acid[4]). These 1,2,3,8-tetrahydro-1,2-dioxocyclobuta[*b*]quinoxalines are readily obtained upon reaction of equimolar quantities of squaric acid, dissolved in hot water, with the appropriate *o*-phenylenediamine, dissolved in hot 25% w/v sulphuric acid. The mixture is heated at 90—100° for 2—3 min. and then allowed to cool to room temperature. The solid reaction product is filtered off and purified with various solvents, and dried *in vacuo* (yields 20% to 50%). These strongly-coloured condensation products are sparingly soluble in most organic solvents. The main features of their i.r. and n.m.r. spectra are summarised in the Table.

The elemental analyses are in agreement with the above formulations. The mass spectra of all these compounds show a parent molecular-ion peak consistent with the empirical formula (the anhydrous molecular-ion peak in the case of the monohydrates). The fragmentation is characterised by the successive elimination of two carbon monoxide fragments followed by two hydrogen cyanide fragments.

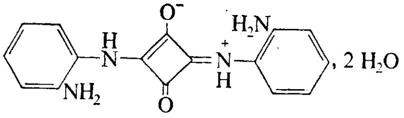
The i.r. spectra show absorption bands in the region 3100 cm.$^{-1}$ to 3200 cm.$^{-1}$ which may be ascribed to the N–H stretching vibrations. Strong sharp carbonyl stretching vibration bands occur at 1795 cm.$^{-1}$ to 1815 cm.$^{-1}$ which are characteristic of the C=O stretching frequencies of cyclobutenediones.[1,5,6]

Further support for the proposed structures is provided by the $^1$H n.m.r. data. All the compounds show that the integrated areas of the aromatic ring-proton signal are in the correct ratio to the two NH-proton signal areas at low field.

In presence of excess of *o*-phenylenediamine, in 10% w/v acetic acid, squaric acid condenses to give a colourless, crystalline solid, which decomposes at 140°, and is soluble in a number of organic solvents. Elemental analysis indicates that a di-condensation product may have been obtained. Its structure may be similar to that proposed for similar condensation products obtained from squaric acid, with primary and secondary aromatic amines.[7]

|  |  |  | I.r. | $^1$H n.m.r. (in DMSO) |  |
|---|---|---|---|---|---|
| R | Decomp.(°) | Properties | $\nu_{C=O}$ (cm.$^{-1}$) | ring H (τ) | NH (τ) |
| H | 330 | dark red solid | 1815<br>1800 | 3·29—3·75 m | 0·04 |
| 5-Me | 280 | brown solid | 1800 | 3·46—3·83 m | 0·08 |
| 5-Me<br>6-Me | 285 | orange solid<br>(monohydrate) | 1808<br>1795 | 3·85 | 0·18 |
| 5-Cl | 305 | brown crystals | 1807 | 3·24—3·40 m | −0·07 |
| 5-$NO_2$ | 290 | dark red-brown solid<br>(monohydrate) | 1800 | 2·33—3·66 m | −0·61<br>−0·31 d |
| 5-$CO_2H$ | >310 | yellow solid<br>(monohydrate) | 1808 | 2·72—3·70 m | −0·26<br>−0·13 d |

The i.r. spectrum shows no carbonyl-stretching vibration band in the cyclobutenedione C=O region. Strong sharp bands occur at 1650 cm.$^{-1}$ and 1615 cm.$^{-1}$. The O–H and N–H stretching vibration region has strong sharp bands at 3450 cm.$^{-1}$, 3350 cm.$^{-1}$, 3240 cm.$^{-1}$, and broader bands at 2850 cm.$^{-1}$ and 2580 cm.$^{-1}$.



The compound was found to complex readily with nickel and copper salts. Further investigations are being undertaken in order to establish the structure of both the metal complexes and the condensation product itself.

S. Skujins gratefully acknowledges the receipt of a University of Surrey Research Studentship.

(*Received, April 2nd,* 1968; *Com.* 411.)

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