Condensations of 3,4-Bis(diphenylmethylene)-1,2-cyclobutanedione with *o*-Phenylenediamine under Ionic and Radical Reaction Conditions

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Synopsis The title condensations under ionic and radical reaction conditions gave 1,2-bis(diphenylmethylene)-1,2-dihydrocyclobuta[*b*]quinoxaline and 7,8-bis(diphenylmethylene)-7,8-dihydrobenzo[*b*][1,4]diazocine-6,9(5*H*,10*H*)-dione respectively.

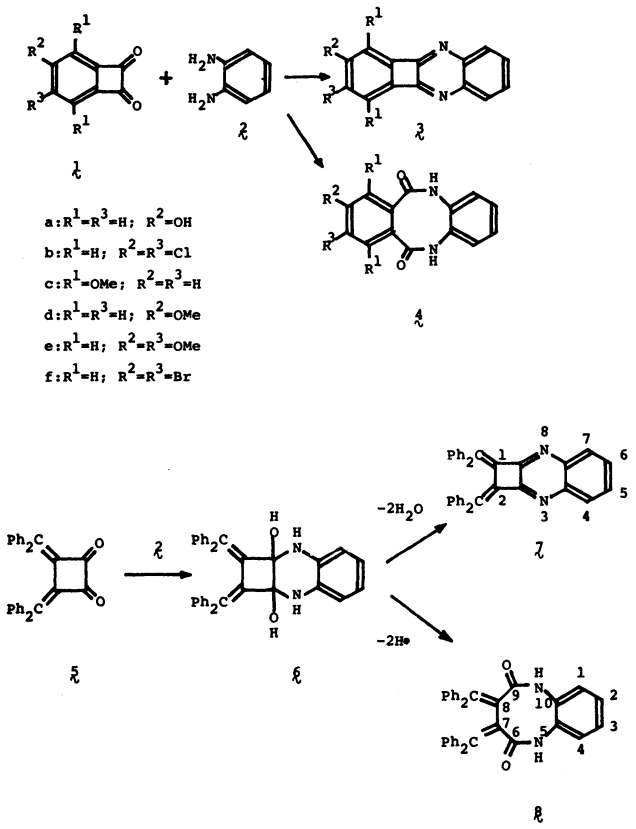
Recently, McOmie and his co-workers have found that the kind of the condensation product of substituted benzocyclobutene-1,2-dione (**1**) with *o*-phenylenediamine (**2**) is very sensitively affected by the substituents of the former. For example, the condensation of **1a—c** with **2** in MeOH containing AcOH gave the corresponding 5,10-diazabenzo[*b*]biphenylenes (**3a—c**), whereas the similar condensation of **1d—f** gave the corresponding dibenzo[*b*,*f*][1,4]diazocine-6,11(5*H*,12*H*)-diones (**4d—f**).[1] However, the reason for the difference has not been clear.

We have now found that the condensations of 3,4-bis(diphenylmethylene)-1,2-cyclobutanedione (**5**) with **2** under ionic and radical reaction conditions gave 1,2-bis(diphenylmethylene)-1,2-dihydrocyclobuta[*b*]quinoxaline (**7**) and 7,8-bis(diphenylmethylene)-7,8-dihydrobenzo[*b*][1,4]diazocine-6,9(5*H*,10*H*)-dione (**8**) respectively. When a solution of **5**[2] and an equimolar amount of **2** in CCl_4 was kept at room temperature for 120 min, **7** and **8** were obtained in 46 and 53% yields respectively (Table 1). When the reaction was carried out in the dark, the yield of **7** increased slightly. The condensation reaction was accelerated by the addition of AcOH. The reaction in CCl_4 containing 3% AcOH ceased within 15 min and gave **7** and **8** in 56 and 43% yields respectively. When the concentration of AcOH was increased to 20 or 50%, the reaction was much more accelerated and gave only **7** in a 98% yield in both cases. The termination of the reaction can easily be followed by observing the disappearance of the deep green color of **5**. The above results clearly show that the acide catalyzed condensation of **5** and **2** gives **7**.

On the contrary, the reaction in the presence of the radical initiator $CBrCl_3$ gave **8** in an 85% yield in addition to a small amount of **7**. When the same reaction was carried out in the dark, however, the yield of **8** decreased to 50% and the yield of **7** increased to 44%. The homolysis of $CBrCl_3$ to trihalomethyl and halogeno radicals is accelerated by light.[3] The formation of **8** by the reaction in CCl_4 in the dark may be due to radical species produced by a dark reaction of **2** and CCl_4, for no reaction occurred in MeOH in the dark.

The plausible reaction pathways are shown in Scheme 1. The reaction of **5** and **2** gives the diol intermediate (**6**), which, upon acid-catalyzed dehydration and radical-induced dehydrogenation, affords **7** and **8** respectively. When the halogeno radical abstracts hydrogen from **6**, **8**, and hydrogen halide are formed. The hydrogen halide thus formed catalyzes the dehydration of **6**. This would be the reason that the formation of **8** always accompanies that of **7**.

Nonetheless, it is not clear whether McOmie's case is similar to ours or not.[4]



Scheme 1.

Table 1. Reaction of **5** with **2** in CCl_4

Additive (v/v%)		Reaction time/min	Yield/%	
			7	**8**
—		120	46	53
—	(dark)	240	51	48
AcOH	3	15	56	43
AcOH	20	10	98	—
AcOH	50	5	98	—
$CBrCl_3$	10	20	14	85
$CBrCl_3$	10 (dark)	40	44	50

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Experimental

Condensation Reaction of 5 with 2 in the Absence of AcOH. When a solution of **5**[2] (0.24 g, 0.58 mmol) and **2** (0.063 g, 0.58 mmol) in CCl_4 (20 ml) was kept at room temperature for 120 min, the deep green color of **5** disappeared completely, resulting in an orange-colored CCl_4 solution. This solution was poured into a column filled with silica gel; it was subsequently eluted by $CHCl_3$ and THF to give **7** as yellow prisms (0.128 g; 46%; mp 240—241 °C (lit,[2] mp 240—241 °C)) and **8** as colorless prisms (0.16 g; 53% mp 287—288 °C) respectively. IR (Nujol) 3170 (NH) and 1660 cm^{-1} (CO). UV ($CHCl_3$) 298 (ε 8300) and 356 nm (3400). MS (75 eV) *m/e* (rel intensity) 518 (M^+; 100), 340(90), and 322(20), ^1H NMR ($CDCl_3$) δ=4.38 (s, NH, 2H) and 6.5—7.6 (m, Ar, 24H).

Found: C, 83.11; H, 5.07; N, 5.29%. Calcd for $C_{36}H_{26}O_2N_2$: C, 83.37; H, 5.05; N, 5.40%.

The reaction mixture obtained by carrying out the reaction in the dark and in the presence of $CBrCl_3$ was treated by the same method as above (Table 1).

Condensation Reaction of 5 with 2 in the Presence of AcOH. The reaction was carried out by a method similar to that used for the reaction in the absence of AcOH. The reaction mixture was washed with aq $NaHCO_3$ and water, and dried over Na_2SO_4. The dried CCl_4 solution was then column-chromatographed on silica gel in the same manner as that described above (Table 1).

References

1) O. Abou-Teim, N. P. Hacker, R. B. Jansen, J. F. W. McOmie, and D. H. Perry, *J. Chem. Soc., Perkin Trans. 1*, **1981**, 988.

2) F. Toda and K. Akagi, *Tetrahedron*, **27**, 2801 (1971).

3) E. S. Huyser, *J. Am. Chem. Soc.*, **82**, 391 (1960).

4) According to our request, McOmie and his co-workers tried their condensation reactions under our reaction conditions, but they could not get clear results; private communication.