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CONDENSATION OF o-PHENYLENEDIAMINE WITH trans-DIBENZOYLETHYLENE

SYNTHESIS OF 2, 5-DIPHENYL-1, 6-DIHYDRO-1, 6-BENZODIAZOCINE

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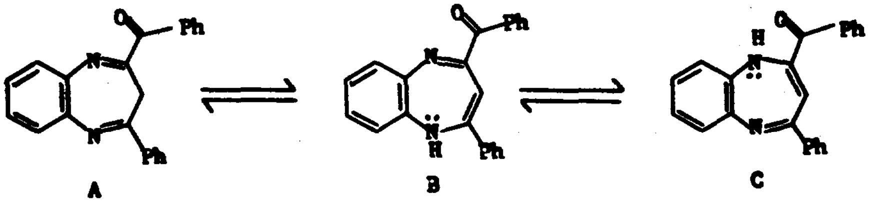
We have reported[2] earlier that aromatic diamines on condensation with dialdehydes furnish the bis-Schiff base products only when the macrocyclic ring is 12-membered or larger, bicyclic hydride shift products being formed when the ring size of the potential bis-Schiff base is smaller than twelve. However, two modes of condensation are possible between aromatic diamines and α,β -unsaturated diketones; a 1, 4 condensation with the formation of a bis-Schiff base or a Michael addition followed by condensation resulting in formation of a 1, 2 or a 1, 3-adduct. We now wish to report the condensation of o-phenylenediamine (1) with 1, 2-dibenzoylethylene (2) which resulted in the formation of two novel heterocycles 6 and 8, whose formation is proposed to involve intermediates that undergo interesting oxidation-reduction reactions. One of these compounds (8) was assigned the wrong structure in an earlier report[3].

Refluxing equimolar amounts of 1 and 2 in acetic acid as described earlier[3] gave a mixture of products from which a colorless crystalline product was obtained (yield 7%, m.p. 203°C) whose UV and IR spectral properties and m.p. were the same as those reported for 2, 5-diphenyl 1, 6-benzodiazocine (3). Mass spectral and elemental analysis data on this compound showed it to have a molecular formula of $C_{22}H_{18}N_2$ which is two hydrogen atoms more than that for 2, 5-diphenyl-1, 6-benzodiazocine (3). The clue to the correct structure was provided by its pmr spectrum which displayed a 2 H singlet at δ 3.5 that disappears on exchange with D_2O. The other signals appear at δ 6·6

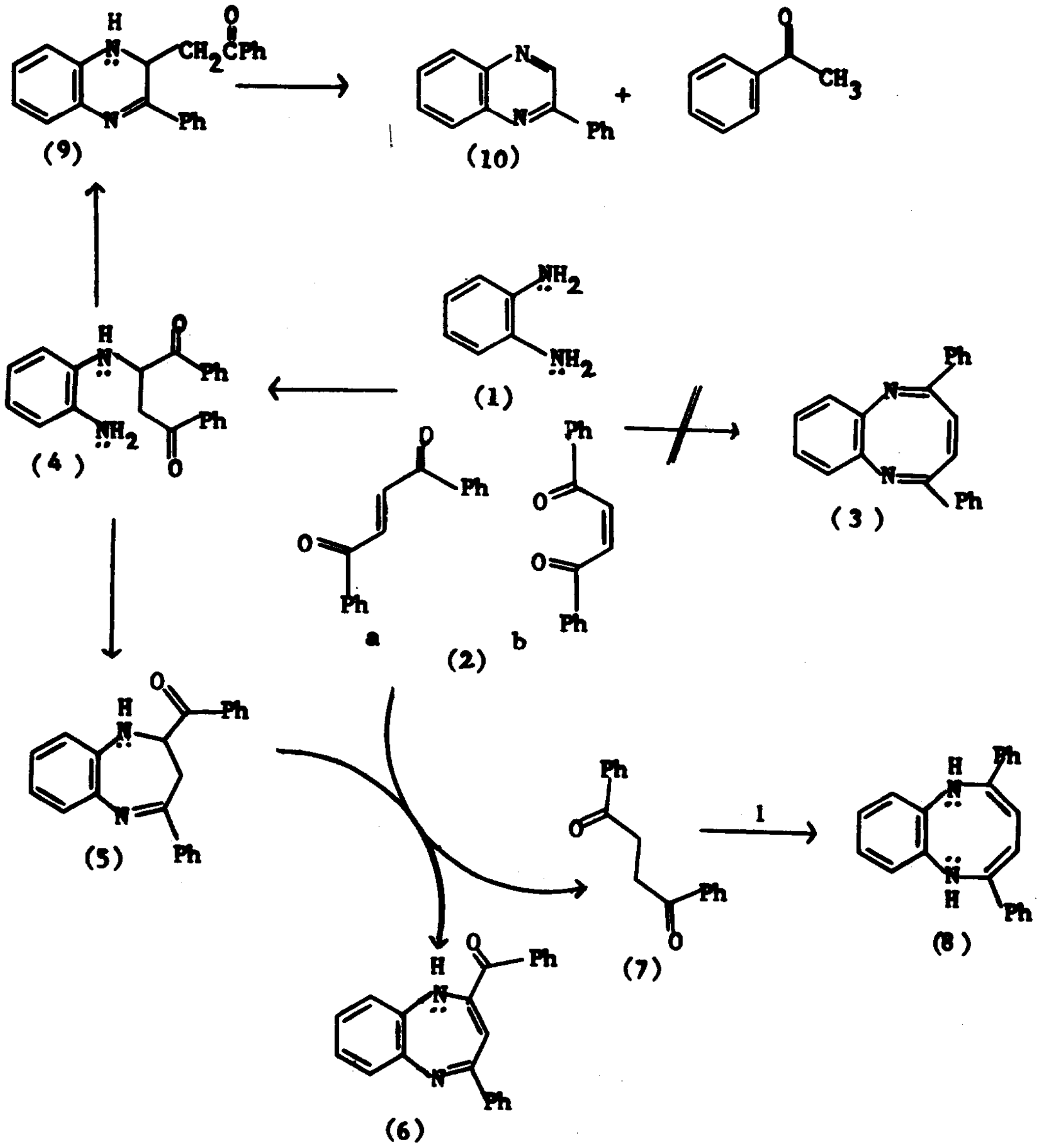
(2H, s, C_3H, C_4H), δ 6·7-7·25 (4H, m, aromatics) and at δ 7·3 (10H, s, aromatics). The IR spectrum displayed N-H absorption at 3400 and 3500 cm^{-1}. On the basis of above data the correct structure was determined to be 2, 5-diphenyl 1,6-dihydro 1,6-benzodiazocine (8). Its UV spectrum showed a long wavelength absorption at 302 nm (cyclohexane, ε = 23,000) indicating the nonplanarity of the molecule. Drieding molecular models showed the molecule to be non-planar with the two nitrogen atoms occurring in two intersecting planes. The corresponding oxygen[4], sulfur[5] and N-methyl[6] analogs also were found to be non aromatic.

The major product of the reaction (36% yield) was isolated as deep orange needles (m.p. 169°C). Its electronic spectrum showed long wavelength absorption in the visible region, λ max 452 nm (cyclohexane, ε = 35,000). The mass spectrum showed a molecular ion peak at m/e 324; the pmr displayed a one proton singlet at δ 6·4 (proton at C_3) and a multiplet between δ 7·2 and 8·05 (15 H, aromatic protons and an NH). From the above spectral data and elemental analysis its structure was deduced to be 2-benzoyl-4-phenyl, (1H) 1,5-benzodiazepine (6). Although 1,5-benzodiazepines are known[7] to exist in the more favorable, colorless form A, in the present case forms B, C appear to be stabilized because of the carbonyl function at the two position.



The other products isolated from the reaction mixture were 1,2-dibenzoylethane (7)[8], 27%; 2-phenylquinoxaline (10)[9], 6%; acetophenone, 6% and unreacted o-phenylenediamine. A different course for the reaction was observed when the reactants were refluxed in ethanol containing 5% acetic acid. 2-Phenylquinoxaline was obtained as the major product (90%). The course of reaction was similar whether cis or trans dibenzoylethylene (2a or 2b) was used.

Scheme I



Any speculations concerning the mechanism of this condensation are by necessity only tentative, since several competing reactions seem to be proceeding simultaneously. However, one of the most interesting questions which arose once the structures of 6 and 8 had been established was how to forward a convincing mechanism to account for the unusual reaction where the product 6 is one oxidation state higher while the product 8 is one oxidation state lower than expected. A feasible mechanism for the reaction is outlined in Scheme I.

The key intermediate involved is the Michael adduct 4 which could undergo Schiff base formation at either of the two carbonyl functions to give the seven membered ring (5) or the dihydroquinoxaline derivative (9) which eliminates an acetophenone moiety to furnish 2-phenylquinoxaline (10). The dihydrobenzodiazepine (5) could undergo dehydrogenation to yield 6. Evidence that dibenzoylethylene (2) plays the dual role of substrate as well as oxidant during the reaction is provided by the isolation of 1, 2-dibenzoylethane (7) as a by-product from the reaction. Moreover, dihydrobenzodiazocine (8) can be prepared by condensation of o-phenylenediamine and 1, 2-dibenzoylethane under the same reaction conditions.

Formation of 2-phenylquinoxaline can also be explained by postulating a Schiff base formation followed by Michael addition β to the carbonyl function.

Further work in the area is now underway.

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