The Reaction of (E,E)-1,4-Dibenzoyl-1,3-butadiene with o-Phenylenediamine

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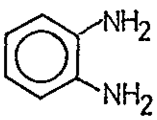
(E,E)-1,4-Dibenzoyl-1,3-butadiene condenses with o-phenylenediamine to give a mixture from which 2-phenylquinoxaline, 1-phenyl-2-buten-1-one and a new compound 2,3-diphenacyl-1,2,3,4-tetrahydroquinoxaline have been isolated. The products are rationalized in terms of initial 1,2- and 1,4-additions plus a retroaldol cleavage.

(E,E)-1,4-Dibenzoyl-1,3-butadiene (I) was first prepared by Klingsberg and coworkers (1) and by Bailey and Ross (2). Bailey and Ross reported several addition reactions of (I) but did not mention any reaction with primary amines. In view of the recent reports (3) of the reaction of 1,2-dibenzoylethylene (II) with o-phenylenediamine (III)(reaction A), we decided to investigate the behavior of (I), which is a vinylog of (II).

(I)

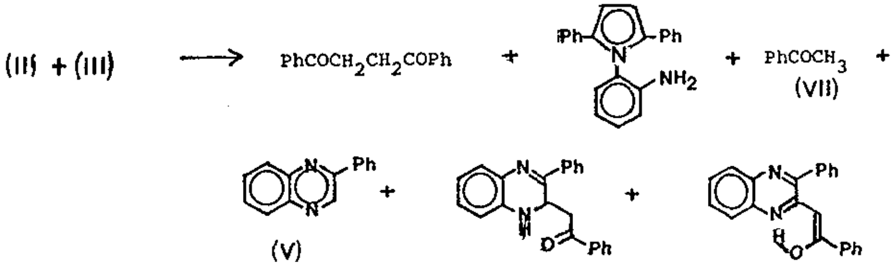
PhCOCH=CHCOPh

(II)



(III)

(A)

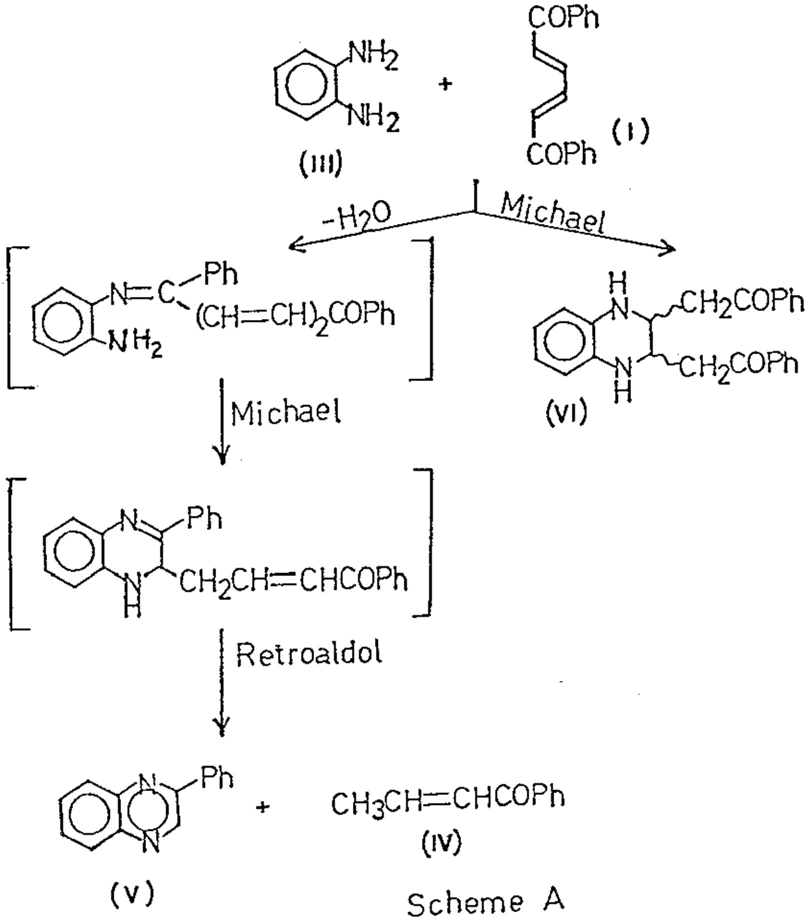


Compound (I) was synthesized from (E,E)-muconic acid using the method of Bailey and Ross (2). In our initial attempts to prepare (I) under the standard fluorescent lighting conditions present in our laboratory, tlc analysis showed that the product had undergone partial photolysis after even short periods of time, either in solution or in the solid state (2,4). We found that even a switch to incandescent illumination did not eliminate this problem. After quickly rejecting the idea of working in complete darkness and investigating several alternatives, we found that the use of gold fluorescent lamps (0% transmission <500 nm) (5) permitted the preparation of pure (I). All experiments involving (I) were performed under such lighting.

A mixture of 627 mg of (I) and 259 mg of (III) in 67 ml of 1-propanol was heated to boiling, whereupon all of the solid dissolved. The solution was refluxed for 32 hours, after which time no further change in the reaction mixture could be detected by tlc, which evinced at least three components in addition to starting material. The cooled reaction mixture was diluted with water and extracted with ether. The ethereal solution yield 826 mg of a dark, sweet-smelling solid. Chromatography on silica gel afforded, in addition to 324 mg of (I), 18 mg of a sweet-smelling oil shown to be 1-phenyl-2-buten-1-one (IV) by comparison with a commercial sample, 38 mg of a solid identified as 2-phenylquinoxaline (V), and 173 mg of a yellow solid, shown by tlc to consist of several compounds (6), including (I). Most of (I) was removed by crystallization, the filtrate being subject to preparative tlc. The major product was 38 mg of a yellow solid (A) mp 221-2° (dec.) shown to be homogeneous on tlc analysis.

Compound (A) was assigned structure (VI)(2,3-diphenacyl-1,2,3,4-tetrahydroquinoxaline) on the basis of its spectra. The ir spectrum evinced secondary amine and carbonyl bands. The 100 MHz ^{1}H n.m.r. spectrum ($CDCl_3$) showed multiplets at δ 7.96 and 7.50 (2 C_6H_5), a symmetrical multiplet at δ 6.54 (o-C_6H_4); a broad resonance at δ 4.36 which disappeared on shaking with D_2O (2NH), and multiplets at δ 3.90 (2 CH) and δ 3.37 (2 CH_2). The mass spectrum of (VI) displayed a M^+ at m/e 370, consistent with the molecular formula of VI (7). Also present were fragments at m/e 251, 250, 145, 132, 131, 105, and 77.

The reaction products and possible intermediates are shown in scheme A. The postulated reaction mechanism is supported by


NH2
NH2
(III)
+
COPh
COPh
(I)
-H2O
Michael
N=C
Ph
(CH=CH)2COPh
NH2
H
N
CH2COPh
N
H
CH2COPh
(VI)
Michael
N
Ph
N
H
CH2CH=CHCOPh
Retroaldol
N
Ph
N
+
CH3CH=CHCOPh
(IV)
(V)

Scheme A

the isolation of similar or identical compounds from the reaction of o-pehnylenediamine with dibenzoylethylene (reaction A)(3). A small amount of acetophenone has been detected when the reaction is run for 80 hours and when solutions of (VI) are allowed to stand for several months. Although we have no evidence for this, a possible mode of formation could be Retroaldol cleavage of (VI).

Further investigation of this and other reactions of (I) is in progress.

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5. Westinghouse lamp no. F 20 T 12/GO "Gold-Bug-A-Way" 20W (24").
6. On all runs, mixtures were obtained that could not be separated chromatographically. These were not further investigated.
7. Elemental analysis was consistent with (VI)($C_{24}H_{22}N_2O_2$).

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