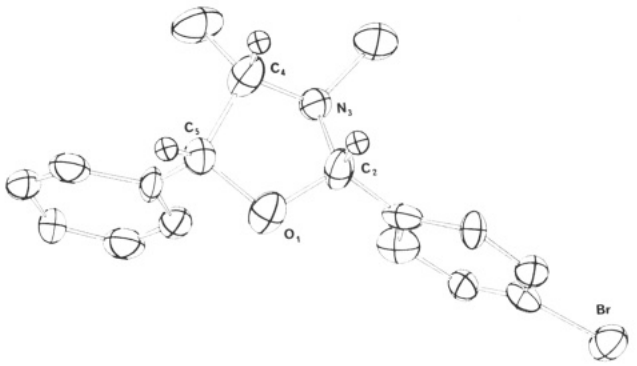

Figure 1. Molecular structure of (2*S*,4*S*,5*R*)-2-(*p*-bromophenyl)-3,4-dimethyl-5-phenyloxazolidine (hydrogen atoms have been placed in calculated positions for clarity; labels in parentheses are conventional).

1 H, H_4), 5.28 (s, 1 H, H_2), 5.50 (d, 1 H, H_5), 7.20–7.60 (m, 9 H, arom).

Structure Determination

Crystal data are as follows: $C_{17}H_{18}BrNO$, fw = 332.239; monoclinic; space group $P2_1$; a = 16.473 (3), b = 8.303 (2), c = 5.668 (3) Å; β = 99.30 (3)°; V = 764.92 Å^3; Z = 2; ρ_{calcd} = 1.443, ρ_{obsd} = 1.45 (2) g cm^{-3} (Mo Kα, λ = 0.710 69 Å, 20°, μ = 26.54 cm^{-1}).

The crystal selected for the structure determination was a thin plate (approximately 0.4 × 0.3 × 0.05 mm). The thinness of the crystals caused rather low intensity diffraction and severely limited the precision of the final structure analysis. Photographic data were used to determine the space group, and intensity data were collected on a Picker FACS-1 diffractometer. A unique quadrant of 783 reflections (3.5° > 20° > 40.0°) yielded 668 with $I > 30(I)$ which were used in the solution by the heavy-atom method and refinement by the block-diaganol least-squares method.[7] All nonhydrogen atoms were included with anisotropic thermal parameters. A final difference Fourier synthesis was devoid of significant features with electron density greater than 0.7 electrons/Å^3. Both enantiomorphs were tested in refinement, yielding final discrepancy indices R_f = 0.0663, R_{wf} = 0.0862 and R_f = 0.0696, R_{wf} = 0.0898 for the expected and opposite enantiomers, respectively. The final coordinates and anisotropic thermal parameters are collected in Table I.[8] A listing of bond lengths and angles may be found in Table II.[8] Figure 1 shows the molecular structure: the key finding is that the bromophenyl group is found on the *same* side of the five-membered ring as the phenyl group and the *C*-methyl group.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

Registry No. **6**, 29863-93-2; **7**, 86392-56-5; *l*-ephedrine, 299-42-3; *p*-bromobenzaldehyde, 1122-91-4.

Supplementary Material Available: A listing of final position and thermal parameters and distances and angles (2 pages). Ordering information is given on any current masthead page.

(7) Data collection operations and all structure solution and refinement were handled by using programs written for the Digital PDP-8a minicomputer by Dr. E. Gabe et al. at the National Research Council, Ottawa, Canada.

(8) See the note on supplementary material at the end of this paper.

New Heterocyclic Syntheses from Benzil Dianils

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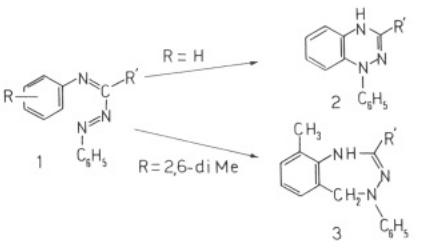
Arylazo imines **1** undergo acid-catalyzed or thermal cyclization to form dihydrobenzo-1,2,4-triazines **2**.[1] If two methyl groups are present in the ortho positions of the aromatic ring bound to the imine nitrogen, dihydrobenzo-1,3,4-triazepines **3**[2] are formed.

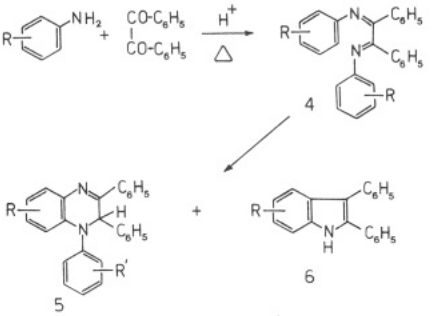


This paper reports the preliminary results of an effort to determine whether similar reactions occur in the case of dianils of α-diketones, in particular of benzil **4**.

Results

The parent compound **4a**, which has been known in the literature for nearly a century, has been prepared under a great variety of experimental conditions from benzil and aniline in the presence of acid catalysts and at high temperatures. Reported yields are generally modest due to concomitant formation of unidentified byproducts characterized by strong green fluorescence in solution.[3]

We have determined that benzil reacts with an excess of aniline, 4-toluidine, or 3,5-dimethylaniline at 200 °C for 3–4 h in the presence of 4-toluenesulfonic acid as catalyst, to give in all cases the corresponding 1,2-dihydroquinoxaline **5** in yields of 30–50%.



4a, R = H
b, R = 4-Me
c, R = 3,5-Me$_2$
d, R = 2,6-Me$_2$

5a, R = R′ = H
b, R = 7-Me; R′ = 4-Me
c, R = 6,8-Me$_2$; R′ = 3,5-Me$_2$

6a, R = 5-Me
b, R = 4,6-Me$_2$

Solutions of **5** in most organic solvents showed a typical blue-green fluorescence.

Concomitant formation of the indole derivatives **6** was observed in two cases, due to partial reduction of benzil to benzoin, possibly involving **5**, which is readily oxidized

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0022-3263/83/1948-2924$01.50/0

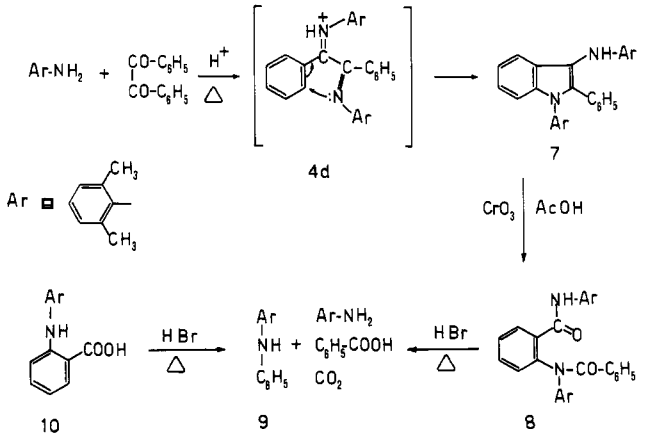
to quinoxalinium salts.[4] In fact, benzoin is known[5] to readily form indoles upon reaction with aromatic amines.

It was further demonstrated that the benzil dianil **4a** is stable at high temperatures but cyclizes rapidly to **5a** upon addition of an acid catalyst. The protonated dianils are thus capable of an electrocyclic reaction to form dihydroquinoxalines **5**.

These results confirm the initial hypothesis and are related to other syntheses of heterocyclic compounds involving the closure of unsaturated conjugated systems containing heteroatoms.[6]

However, dihydroquinoxaline **5** cannot form when the ortho positions of the aromatic amine are occupied: the reaction between benzil and 2,6-xylidine at 200 °C for 20 h in the presence of an acid catalyst gives a more than 60% yield of 1-(2,6-dimethylphenyl)-3-[(2,6-dimethylphenyl)amino]-2-phenylindole (**7**).

The structure of the latter was demonstrated through the reactions reported below, involving a typical degradation of the indole system.[7]



The indole **7** is formed from the protonated dianil intermediate **4d**: protonation of a ketimine group leads to electronic deficiency in the phenyl group attached to it, thus making it prone to nucleophilic attack by the second imine nitrogen. In this case, the behavior of dianil is substantially different from that of the corresponding arylazo imines.

Experimental Section

All melting points were determined on a Büchi apparatus and are uncorrected. NMR spectra were recorded on a Varian EM-390 spectrometer with $CDCl_3$ as solvent and with tetramethylsilane as internal standard.

General Procedure for the Synthesis of 5, 6, and 7 from Aromatic Amines and Benzil. A mixture of benzil and a 5-fold excess in weight of the appropriate arylamine was heated at reflux temperature in the presence of catalytic amounts of 4-toluenesulfonic acid. The water formed was continuously distilled off. The crude reaction mixture was extracted with 5% HCl solution to remove unreacted amine and then chromatographed on a silica gel column using $CHCl_3$ as an eluent; under these conditions indoles **6** are eluted before dihydroquinoxalines **5**.

1,2-Dihydro-1,2,3-triphenylquinoxaline (5a): yield 31%. Physical, analytic, and spectral data were identical with those shown by a sample of **5a** prepared according to the literature:[8] mp 104 °C (*i*-PrOH) (lit.[8] mp 116–117 °C); ^1H NMR δ 8.0 (2 H, m, aromatic in position 2 and 6 of the phenyl group in position 3), 7.1 (17 H, m, aromatic), 6.02 (1 H, s, CHN); mol wt (MS) 360. Anal. Calcd for $C_{26}H_{20}N_2$: C, 86.63; H, 5.59; N, 7.77. Found: C, 86.35; H, 5.50; N, 7.52.

1,2-Dihydro-2,3-diphenyl-7-methyl-1-(4-methylphenyl)-quinoxaline (5b): yield 55%; mp 155 °C (*n*-hexane); ^1H NMR δ 8.0 (2 H, m, aromatic in position 2 and 6 of the phenyl group in position 3), 6.8 (2 H, m, aromatic in position 2 and 6 of the 4-methylphenyl group in position 1), 7.2 (13 H, m, aromatic), 6.0 (1 H, s, CHN), 2.28 and 2.35 (2 × 3 H, 2 s, 2 CH_3); mol wt (MS) 388. Anal. Calcd for $C_{28}H_{24}N_2$: C, 86.56; H, 6.23; N, 7.21. Found: C, 86.76; H, 6.41; N, 6.81.

1,2-Dihydro-6,8-dimethyl-1-(3,5-dimethylphenyl)-2,3-diphenylquinoxaline (5c): yield 27%; mp 150 °C (*n*-hexane); ^1H NMR δ 8.0 (2 H, m, aromatic in position 2 and 6 of the phenyl group in position 3), 6.80 (1 H, s, aromatic in position 6), 6.65 (3 H, s, aromatic of 3,5-dimethylphenyl group in position 1), 7.30 (9 H, m, aromatic), 6.20 (1 H, s, CHN), 2.26 (6 H, s, 2 CH_3 of the 3,5-dimethylphenyl group), 1.95 and 2.33 (2 × 3 H, 2 s, 2 CH_3 in position 6 and 8). Anal. Calcd for $C_{30}H_{28}N_2$: C, 86.50; H, 6.78; N, 6.73. Found: C, 86.24; H, 6.80; N, 6.83.

2,3-Diphenyl-5-methylindole (6b): yield 27%; mp 151 °C (cyclohexane) (lit.[9] mp 152 °C); ^1H NMR (Me_2SO) was in agreement with that described in the literature;[10] mol wt (MS) 267. Anal. Calcd for $C_{21}H_{17}N$: C, 89.01; H, 6.05; N, 4.94. Found: C, 89.04; H, 6.05; N, 4.81.

2,3-Diphenyl-4,6-dimethylindole (6c): yield 32%; mp 131–132 °C (lit.[11] 131–132 °C); ^1H NMR δ 8.20 (1 H, br s, NH), 7.30 and 7.40 (2 m, 2 × 5 H, C_6H_5), 7.10 (1 H, s, aromatic in position 7), 6.72 (1 H, s, aromatic in position 5), 2.11 and 2.50 (2 s, 2 × 3 H, 2 CH_3). Anal. Calcd for $C_{22}H_{19}N$: C, 88.85; H, 6.44; N, 4.71. Found: C, 88.65; H, 6.47; N, 4.65.

1-(2,6-Dimethylphenyl)-3-[(2,6-dimethylphenyl)amino]-2-phenylindole (7); reaction time, 12 h; mp 179 °C (*i*-PrOH); yield 67%; ^1H NMR δ 1.98 (6 H, s, 2 CH_3 of 2,6-dimethylanilino group in position 3), 2.20 (6 H, s, 2 CH_3 of 2,6-dimethylphenyl group in position 1), 5.20 (1 H, br s exchangeable with D_2O, NH), 7.20 (15 H, m, aromatic); mol wt (MS) 416. Anal. Calcd for $C_{30}H_{28}N_2$: C, 86.54; H, 6.73; N, 6.73. Found: C, 86.61; H, 6.81; N, 6.51.

Oxidation of 7. A solution of CrO_3 (5 g) in H_2O (5 mL) was added dropwise to a solution of **7** (5 g) in glacial AcOH (100 mL). After the exothermic reaction subsided, the mixture was maintained at 80 °C for 10 min. The solvent was then removed under reduced pressure and the residue treated with H_2O and $CHCl_3$. The organic layer was dried over Na_2SO_4 and evaporated to give a solid, which was triturated with C_6H_6 and then crystallized from $AcOH/H_2O$ to give **N′-benzoyl-N,N′-bis(2,6-dimethylphenyl)anthranilamide (8)**: mp 254 °C (Köfler) (3.0 g); NMR δ 2.18 (12 H, m, 4 CH_3), 7.33 [16 H (1 H exchangeable with D_2O), m, aromatic and NH]; mol wt (MS) 448. Anal. Calcd for $C_{30}H_{28}N_2O_2$: C, 80.33; H, 6.30; N, 6.25. Found: C, 79.92; H, 6.12; N, 6.22. Hydrolysis of **8** in refluxing 48% HBr–AcOH (1:1) solution (2 h) gave, after the usual workup, 2,6-dimethylaniline (isolated as the benzoyl derivative), benzoic acid, and *N*-phenyl-2,6-dimethylaniline (**9**),[12] identical with an authentic sample obtained by decarboxylation of *N*-(2,6-dimethylphenyl)anthranilic acid in refluxing 48% HBr (2 h).

Acknowledgment. I am grateful to Professor Raffaello Fusco for his helpful advice and participation.

Registry No. **5a**, 86365-64-2; **5b**, 86365-65-3; **5c**, 86365-66-4; **6b**, 36804-50-9; **6c**, 3469-20-3; **7**, 86365-67-5; **8**, 86365-68-6; aniline, 62-53-3; 4-methylaniline, 106-49-0; 3,5-dimethylaniline, 108-69-0; 2,6-dimethylaniline, 87-62-7; benzil, 134-81-6; 4-methylbenzenesulfonic acid, 104-15-4.

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