Synthesis of 2-(*p*-R-Benzoylmethylene)-3-(*p*-R-phenyl)-1*H*-quinoxalines

Braulio Insuasty*, Fernando Fernández, Jairo Quiroga and Rodolfo Moreno

Departamento de Química, Universidad del Valle, A. A. 25360, Cali, Colombia

Roberto Martínez, Enrique Angeles and Rubén Gaviño

Instituto de Química y FES-Cuautitlán, Universidad Nacional Autónoma de México, Circuito exterior, Ciudad Universitaria, Coyoacán 04510, México DF

Regina H. de Almeida S.

Instituto de Química de Sao Carlos, USP, CP 780 Sao Carlos, Brasil

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The reaction of 1,2-diaminobenzenes with substituted 1,2-dibenzoyl-1,2-dibromoethanes constitutes a convenient synthetic route to the hitherto 2-(*p*-R-benzoylmethylene)-3-(*p*-R-phenyl)-1*H*-quinoxalines. Structures of all products were elucidated by ir, ^{1}H and ^{13}C-nmr, mass spectra data. X-Ray crystallography data confirm assigned structures.

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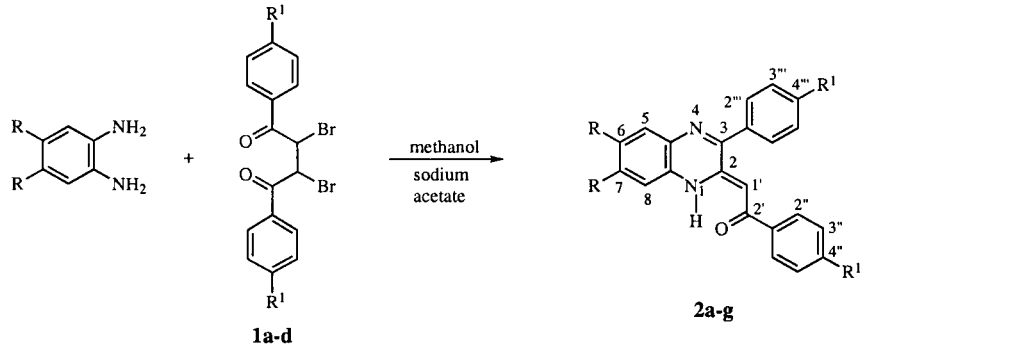
It is well known that the reaction between α-haloketones and 1,2-diamines produces derivatives of six-member heterocyclic rings [1-3]. For instance, the 1,2-diaminobenzenes with 2-bromo-1,3-diaryl-1-propanones give 3-aryl-2-benzyl-1,2-dihydroquinoxalines [4]. The purpose of this work was to explore the reaction of 1,2-diaminobenzene and 1,2-diamino-4,5-dimethylbenzene with substituted 1,2-dibenzoyl-1,2-dibromoethanes (Scheme 1). In a typical procedure, 1,2-diaminobenzene, 1,2-dibenzoyl-1,2-dibromoethane **1a** and sodium acetate were refluxed in methanol to give **2a**. The infrared spectrum of **2a** displayed absorption at 3350 and 1594 cm^{-1}, assigned to NH and C=O stretching, respectively; the uv/visible spectrum of **2a** in methanol contains five bands in the range of 213-457 nm (Table 1). The mass spectrum shows ions at m/z 219 (M-105) and m/z 105, consistent with the presence of the PhCO moiety in the framework of **2a**. The ^{1}H nmr spectrum of **2a** showed typical signals

Scheme 1



1a-d **2a-g**

Table 1

Physicochemical Properties of Compounds **2a-g**

Compound	R	R^1	uv/vis (ethanol), λ_{nm}	ir (cm^{-1}) $\nu_{C=O}$	Yield (%)	mp °C
2a	H	H	213, 252, 338, 438, 457	1594	23	208-210
2b	H	Me	212, 238, 329, 433, 456	1587	23	181-183
2c	H	Cl	212, 238, 329, 433, 454	1593	18	260-262
2d	H	Br	211, 240, 331, 431, 457	1584	23	281-283
2e	Me	Me	212, 264, 345, 430, 461	1609	16	162-163
2f	Me	Cl	213, 266, 346, 430, 463	1592	25	246-248
2g	Me	Br	213, 267, 340, 430, 465	1585	21	252-254

for the quinoxaline skeleton: two singlets (one proton each) at δ 4.72 and 6.39 ppm, for the protons joined to NH and C1' whereas a multiplet between δ 6.88-7.91 ppm was asigned to the aromatic proton (Table 2). The ^{13}C-

Table 2

^1H NMR Chemical Shifts (δ) for Compounds **2a-g** (deuteriochloroform, 300 MHz)

Compound	N-H	C-H	CH_3	Ar-H
2a	4.72	6.93		6.88-7.91
2b	4.80	6.40	2.35, 2.45	7.12-7.90
2c	4.69	6.24		7.23-7.90
2d	4.66	6.26		7.29-7.91
2e	4.68	6.38	2.35, 2.50	7.14-8.06
2f	4.63	6.23	2.35, 2.55	7.26-7.89
2g	4.65	6.25	2.41, 2.45	7.35-7.90

nmr spectrum showed 18 signals and DEPT experiment indicated that eleven of them correspond to CH and seven to Cq. ^1H-^{13}C correlation (HETCOR) allowed us to identify twelve signals: δ 90.3 (C-1'), 114.3 (C-3), 124.3 (C-6), 125.2 (C-7), 128.3 (C-3'''), 128.6 (C-2'''), 128.8 (C-2''), 129.0 (C-3''), 129.8 (C-4'''), 130.0 (C-5), 130.2 (C-4'') and 183.2 (C=O, ketone) ppm. All the above data agree with the structure of 2-benzoylmethylene-3-phenyl-1*H*-quinoxaline **2a**. Definitive evidence for the structure of the compound **2a** was achieved by single-crystal X-ray diffraction analysis of a single crystal. Figure 1 shows a perspective

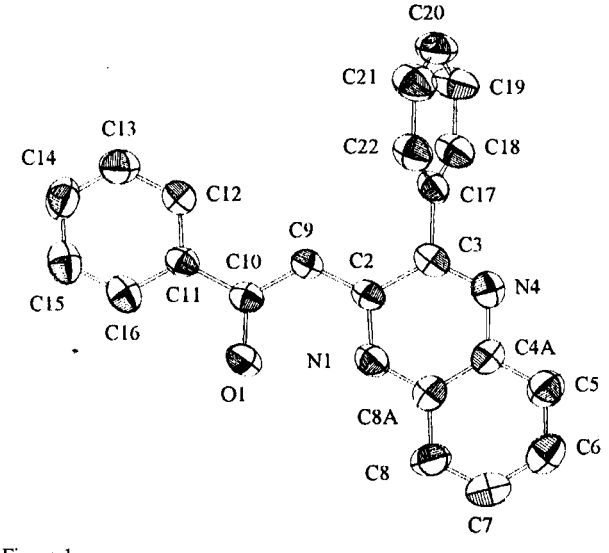


Figure 1.

and atom labelling of **2a**. Bond lengths and angles are shown in Tables 5. The most interesting feature of the crystallographic data is that there is a double bond exocyclic to C-2 and a hydrogen bond between the ketone carbonyl group and the hydrogen of N-1. The general run of this reaction was tested with the 1,2-diaminobenzene and 1,2-di(*p*-R-benzoyl)-1,2-dibromoethanes **1b-d** (R =

Table 3

Crystal Data, Details of Data-collection and Structure Refinement for 2-Benzoylmethylene-3-phenyl-1*H*-quinoxaline **2a**

Crystal Data

Empirical formula	$C_{22}H_{16}N_2O$
MoK_α radiation	λ = 0.71073(Å)
Formula weight	324.37
Temperature	293(2) K
Crystal system	Monoclinic
Space group	$P2_1/c$
cell parameters from 25 reflections	θ = 8.30-18.08°
a = 10.9050(10) (Å)	Prisms
b = 5.830(2) (Å)	Orange
c = 26.150(2) (Å)	0.20 x 0.10 x 0.10 mm
β = 95.6390(3)	D_x = 1.302 (Mg m^{-3})
V = 1654.3(6)	Z = 4
Absorption coefficient	0.081 mm^{-1}

Data collection

Nonius CAD-4 diffractometer	R_{int} = 0.0828
ω/2θ scans	θ_{max} = 24.63°
Absorption correction: none	h = -12→0
2949 Measured reflections	k = 0→6
2791 Independent reflections	l = -30→30
907 observed reflections	3 standard reflections
[I> 3σ(I)]	frequency: 120 minutes
	intensity variation: 1.51%

Refinement

Refinement method	Full-matrix least-squares on F^2
$R(F)$ = 0.0416	$\Delta\rho_{max}$ = 0.130 e $(Å)^{-3}$
$wR(F^2)$ = 0.1090	$\Delta\rho_{min}$ = -0.130 e $(Å)^{-3}$
Goodness-of-fit on F^2 = 0.942	Extinction correction: SHELXL93
227 refined parameters	Extinction coefficient = 0.011(3)
	Atomic scattering factors from
H-atom parameters not refined	International Tables for X-ray
	Crystallography, 1974, Vol **IV**,
$(\Delta/\sigma)_{max} < 0.002$	Table 2.2B

Table 4

Fractional Atomic Coordinates and Isotropic Displacement Parameters of the 2-Benzoylmethylene-3-phenyl-1*H*-quinoxaline

Atom	X/A	Y/B	Z/C	Biso
O1	0.3158(4)	-0.2727(8)	0.7979(1)	4.7(2)
N1	0.4191(5)	0.0712(9)	0.8479(2)	4.1(2)
N4	0.4267(5)	0.358(1)	0.9322(2)	4.2(2)
C2	0.3454(5)	0.023(1)	0.8848(2)	3.4(2)
C3	0.3560(5)	0.176(1)	0.9289(2)	3.6(2)
C4A	0.4979(6)	0.403(1)	0.8921(3)	4.0(2)
C5	0.5732(6)	0.595(1)	0.8941(3)	4.9(3)
C6	0.6433(6)	0.641(1)	0.8550(3)	5.6(3)
C7	0.6418(6)	0.492(1)	0.8130(3)	5.6(3)
C8	0.5689(6)	0.302(1)	0.8103(3)	5.2(3)
C8A	0.4956(6)	0.257(1)	0.8495(2)	3.8(2)
C9	0.2614(5)	-0.157(1)	0.8784(2)	3.8(2)
C10	0.2473(5)	-0.295(1)	0.8346(2)	3.6(2)
C11	0.1508(5)	-0.477(1)	0.8284(2)	3.5(2)
C12	0.0479(6)	-0.470(1)	0.8554(2)	4.4(3)
C13	-0.0406(6)	-0.639(1)	0.8477(3)	5.2(3)
C14	-0.0268(7)	-0.814(1)	0.8139(3)	5.6(3)
C15	0.0756(7)	-0.823(1)	0.7870(2)	5.1(3)
C16	0.1632(6)	-0.655(1)	0.7941(2)	4.4(2)
C17	0.2822(6)	0.131(1)	0.9725(2)	3.7(2)

Table 4 (continued)

Atom	X/A	Y/B	Z/C	Biso
C18	0.1965(6)	0.292(1)	0.9856(2)	4.7(3)
C19	0.1249(7)	0.251(1)	1.0252(2)	5.5(3)
C20	0.1389(7)	0.053(1)	1.0530(3)	5.4(3)
C21	0.2257(7)	-0.108(1)	1.0413(2)	5.4(3)
C22	0.2951(6)	-0.070(1)	1.0013(2)	4.6(3)
HN1	0.4181(5)	-0.0197(9)	0.8220(2)	5.9999(0)
H5	0.5760(6)	0.693(1)	0.9223(3)	5.9999(0)
H6	0.6924(6)	0.772(1)	0.8562(3)	5.9999(0)
H7	0.6909(6)	0.523(1)	0.7867(3)	5.9999(0)
H8	0.5683(6)	0.204(1)	0.7824(3)	5.9999(0)
H9	0.2120(5)	-0.186(1)	0.9047(2)	5.9999(0)
H12	0.0384(6)	-0.353(1)	0.8787(2)	5.9999(0)
H13	-0.1102(6)	-0.634(1)	0.8656(3)	5.9999(0)
H14	-0.0867(7)	-0.928(1)	0.8091(3)	5.9999(0)
H15	0.0852(7)	-0.943(1)	0.7642(2)	5.9999(0)
H16	0.2319(6)	-0.660(1)	0.7757(2)	5.9999(0)
H18	0.1875(6)	0.429(1)	0.9675(2)	5.9999(0)
H19	0.0666(7)	0.358(1)	1.0330(2)	5.9999(0)
H20	0.0905(7)	0.027(1)	1.0798(3)	5.9999(0)
H21	0.2366(7)	-0.242(1)	1.0606(2)	5.9999(0)
H22	0.3518(6)	-0.180(1)	0.9931(2)	5.9999(0)

Table 5

Selected Geometric Parameters of the 2-Benzoylmethylene-3-phenyl-1*H*-quinoxaline

O1	-	C10	1.279(7)		
N1	-	C2	1.345(8)		
N1	-	C8A	1.367(9)		
N4	-	C3	1.309(9)		
N4	-	C4A	1.389(8)		
C2	-	C3	1.454(8)		
C2	-	C9	1.390(9)		
C3	-	C17	1.483(8)		
C4A	-	C5	1.38(1)		
C4A	-	C8A	1.399(9)		
C5	-	C6	1.36(1)		
C6	-	C7	1.40(1)		
C7	-	C8	1.36(1)		
C8	-	C8A	1.386(9)		
C9	-	C10	1.396(8)		
C10	-	C11	1.493(9)		
C11	-	C12	1.385(8)		
C11	-	C16	1.387(9)		
C12	-	C13	1.38(1)		
C13	-	C14	1.37(1)		
C14	-	C15	1.38(1)		
C15	-	C16	1.37(1)		
C17	-	C18	1.391(9)		
C17	-	C22	1.391(9)		
C18	-	C19	1.378(9)		
C19	-	C20	1.36(1)		
C20	-	C21	1.39(1)		
C21	-	C22	1.370(9)		
C2	-	N1	-	C8A	123.3(5)
C3	-	N4	-	C4A	118.3(5)
N1	-	C2	-	C3	115.7(5)
N1	-	C2	-	C9	120.3(5)
C3	-	C2	-	C9	123.9(5)
N4	-	C3	-	C2	123.4(6)
N4	-	C3	-	C17	117.1(5)
C2	-	C3	-	C17	119.5(5)
N4	-	C4A	-	C5	119.9(6)
N4	-	C4A	-	C8A	121.2(6)
C5	-	C4A	-	C8A	119.0(6)
C4A	-	C5	-	C6	120.3(6)
C5	-	C6	-	C7	120.2(7)
C6	-	C7	-	C8	120.4(7)
C7	-	C8	-	C8A	119.5(7)
N1	-	C8A	-	C4A	118.1(6)
N1	-	C8A	-	C8	121.5(6)
C4A	-	C8A	-	C8	120.5(6)
C2	-	C9	-	C10	123.4(6)
O1	-	C10	-	C9	122.2(5)
O1	-	C10	-	C11	116.6(5)
C9	-	C10	-	C11	121.2(5)
C10	-	C11	-	C12	121.6(5)
C10	-	C11	-	C16	119.4(5)
C12	-	C11	-	C16	119.0(6)
C11	-	C12	-	C13	119.9(6)
C12	-	C13	-	C14	120.4(7)
C13	-	C14	-	C15	120.2(7)
C14	-	C15	-	C16	119.7(7)
C11	-	C16	-	C15	120.8(6)
C3	-	C17	-	C18	119.8(5)
C3	-	C17	-	C22	122.2(6)
C18	-	C17	-	C22	118.0(6)
C17	-	C18	-	C19	120.8(6)
C18	-	C19	-	C20	120.4(7)
C19	-	C20	-	C21	119.9(7)
C20	-	C21	-	C22	119.7(6)
C17	-	C22	-	C21	121.2(6)

Table 6

Anisotropic Thermal Parameters of the 2-Benzoylmethylene-3-phenyl-1*H*-quinoxaline

Atom	U(1,1)	U(2,2)	U(3,3)	U(2,3)	U(1,3)	U(1,2)
O1	0.075(3)	0.059(3)	0.049(2)	-0.011(2)	0.021(2)	-0.003(3)
N1	0.060(3)	0.051(4)	0.047(3)	-0.007(3)	0.011(3)	0.003(3)
N4	0.056(3)	0.049(4)	0.054(3)	-0.005(3)	0.003(3)	0.002(3)
C2	0.053(4)	0.041(5)	0.035(3)	0.001(3)	0.009(3)	0.006(4)
C3	0.050(4)	0.046(5)	0.040(4)	0.001(4)	0.003(3)	0.013(4)
C4A	0.046(4)	0.048(5)	0.056(4)	0.004(4)	0.003(3)	-0.006(4)
C5	0.055(5)	0.063(6)	0.070(5)	-0.001(4)	0.007(4)	-0.003(4)
C6	0.065(5)	0.059(6)	0.088(5)	0.004(5)	0.008(5)	-0.010(5)
C7	0.059(5)	0.081(7)	0.076(5)	0.011(5)	0.020(4)	0.000(5)
C8	0.055(4)	0.081(6)	0.064(4)	0.004(5)	0.017(4)	-0.010(5)
C8A	0.047(4)	0.042(4)	0.055(4)	0.005(4)	0.003(3)	0.003(4)
C9	0.058(4)	0.047(4)	0.040(4)	-0.004(4)	0.013(3)	-0.006(4)
C10	0.048(4)	0.046(5)	0.043(4)	0.001(3)	0.008(3)	0.006(3)
C11	0.051(4)	0.048(5)	0.034(4)	0.005(3)	0.004(3)	0.004(4)
C12	0.061(4)	0.059(5)	0.047(4)	-0.005(4)	0.007(3)	-0.007(4)
C13	0.068(5)	0.075(6)	0.057(4)	0.005(5)	0.014(4)	-0.002(5)
C14	0.089(6)	0.054(6)	0.067(5)	0.003(4)	0.000(4)	-0.021(5)
C15	0.080(5)	0.049(5)	0.060(5)	-0.003(4)	-0.005(4)	0.002(5)
C16	0.065(5)	0.051(5)	0.053(4)	-0.006(4)	0.004(3)	0.007(4)
C17	0.068(4)	0.037(4)	0.036(3)	-0.004(3)	0.009(3)	0.001(4)
C18	0.089(5)	0.043(5)	0.048(4)	0.005(4)	0.017(4)	0.011(4)
C19	0.092(6)	0.063(5)	0.058(4)	0.009(4)	0.033(4)	0.020(5)
C20	0.098(6)	0.060(5)	0.054(4)	0.003(4)	0.032(4)	-0.007(5)
C21	0.099(6)	0.058(5)	0.051(4)	0.011(4)	0.016(4)	0.005(5)
C22	0.085(5)	0.036(5)	0.056(4)	-0.001(4)	0.020(4)	0.009(4)
HN1	0.0760(0)					

Me, Cl, Br) that were treated as was compound **1a** and they also afforded **2b-d** as the only products. The ring cyclization of the 1,2-diamino-4,5-dimethylbenzene and the 1,2-di(*p*-R-benzoyl)-1,2-dibromoethanes **1e-g** (R = CH_3, Cl, Br) under similar conditions as for **1a** gave the 6,7-dimethyl-1*H*-quinoxalines **2e-g**. In the infrared spectra of **2e**, bands at 3350 and 1609 cm^{-1} are consistent with the presence of an enaminone group [5]. In agreement with the suggested structure the ^{1}H-nmr spectra of compound **2e** exhibited two up-field signals (three protons each) at δ 2.35 and 2.50 ppm ascribed to the methyl protons of C-6 and C-7; one-proton signals at δ 4.68 and 6.38 ppm for the protons bonded to NH and C-1', and a multiplet in the range δ 7.14-8.06 ppm for the aromatic protons. The ^{1}H-nmr data for all the products are summarized in Table 2. The mass spectra of these compounds showed the corresponding molecular ions and fragments consistent with the assigned structure. The ^{13}C-nmr spectra of compounds **2b-g** were similar to that shown by compound **2a** and are not discussed.

EXPERIMENTAL

All melting points are uncorrected. The ir spectra were recorded on an ATI-Mattson spectrophotometer. The uv-vis spectra in ethanol, were recorded on a Shimadzu UV-160 A spectrophotometer. The ^{1}H-, ^{13}C and ^{1}H-^{13}C nmr spectra were determined in Varian Gemini 200 and Varian-VXR-300S spectrometers. All nmr spectra were obtained with the pulse sequence as part of spectrometer software and were determined in chloroform-d solution containing tetramethylsilane as the internal standard with chemical shifts (δ) expressed downfield from tetramethylsilane. Mass spectra were obtained with a Jeol SX-100 mass spectrometer. Elemental analysis was done on a LECO CHNS-900 analyzer.

Crystal data for **2a** are: $C_{22}H_{16}N_2O$, M = 324.37, monoclinic space group $P2_1/c$, a = 10.905(10), b = 5.830(2), c = 26.150(2) Å, β = 95.64(3), V = 1654.3(6), Z = 4, D_x = 1.302 g•cm^{-3}, μ = 0.081 mm^{-1} (Mo-Kα). Intensities were recorded for 2791 unique reflections by an ω/2Θ scan, $2\Theta_{max}$ 50° on a Nonius CAD-4 at 293 K. Intensity data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and full-matrix least squares refinement with SHELXL93 converged at R = 0.0416, wR = 0.1090 for 227 parameters. The non-H atoms were given anisotropic temperature factors and the H-atoms were added at idealized positions with common fixed isotropic temperature factor U = 0.06 $Å^2$. At convergence $(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ + 0.130, -0.130 e $Å^{-3}$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Center. See Notice to Authors, Issue No. 1.

2-(*p*-R-benzoylmethylene)-3-(*p*-R-phenyl)-1*H*-quinoxalines **2a-g**.

General Procedure (R = H).

A solution of 1,2-diaminobenzene (0.27 g, 2.2 mmoles), 1,2-dibenzoyl-1,2-dibromoethane **1a** (0.79 g, 2.0 mmoles) and sodium acetate (0.16 g, 2.0 mmoles) was refluxed in 40 ml anhydrous methanol for 6 hours. The precipitate was collected by filtration. The solid obtained was recrystallized from acetone to give 0.15 g (23%) of **2a** mp 208-210°. The yields and the melting points are summarized in Table 1.

2-Benzoylmethylene-3-phenyl-1*H*-quinoxaline **2a**.

This compound had ms: EI m,/z (relative abundance) 324 (M^+, 53), 219 (38), 105 (100); ^{13}C nmr (deuteriochloroform): δ 183.2 (C2'=O), 162.0, 147.0, 136.5, 136.4, 131.3, 131.2, 130.2 (C-4"), 130.0 (C-5), 129.8 (C-4'"), 129.0 (C-3"), 128.8 (C-2"), 128.6 (C-2'") 128.3 (C-3'"), 125.2 (C-7), 124.3 (C-6), 114.3 (C-8), 90.3 (C-1').

Anal. Calcd. for $C_{22}H_{16}N_2O$: C, 81.46; H, 4.97; N, 8.63. Found: C, 81.28; H, 4.98; N, 8.72.

2-(*p*-Methylbenzoylmethylene)-3-(*p*-methylphenyl)-1*H*-quinoxaline **2b**.

This compound had ms: El m/z (relative abundance) 352 (M^+, 53), 233 (62), 119 (100); ^{13}C nmr: δ 182.3 (C2'=O), 157.3, 147.0, 137.2, 135.9, 131.6, 130.0, 142.3 (C-4"), 129.5 (C-5), 140.0 (C-4'"), 129.0 (C-3"), 128.3 (C-2"), 128.0 (C-2'"), 127.8 (C-3'"), 126.6 (C-7), 124.6 (C-6), 119.5 (C-8), 90.2 (C-1'), 21.2 and 20.9 (*p*-CH_3-).

Anal. Calcd. for $C_{24}H_{20}N_2O$: C, 81.79; H, 5.72; N, 7.95. Found: C, 82.15; H, 5.63; N, 7.98.

2-(*p*-Chlorobenzoylmethylene)-3-(*p*-chlorophenyl)-1*H*-quinoxaline **2c**.

This compound had ms: EI m/z (relative abundance) 392 (M^+, 54), 253 (50), 139 (100); ^{13}C nmr: δ 181.3 (C-2'), 161.2, 145.3, 136.0, 136.5, 132.0, 131.2, 139.2 (C-4"), 130.1 (C-5), 135.2 (C-4'"), 129.6 (C-3"), 131.1 (C-2"), 127.2 (C-2'"), 128.2 (C-3'"), 125.5 (C-7), 124.5 (C-6), 117.3 (C-8), 90.7 (C-1').

Anal. Calcd. for $C_{22}H_{14}N_2OCl_2$: C, 67.19; H, 3.58; N, 7.13. Found: C, 67.25; H, 3.47; N, 7.17.

2-(*p*-Bromobenzoylmethylene)-3-(*p*-bromophenyl)-1*H*-quinoxaline **2d**.

This compound had ms: EI m/z (relative abundance) 480 (M^+, 63), 297 (32), 183 (100); ^{13}C nmr: δ 182.2 (C2'), 162.3, 148.1, 136.2, 136.8, 132.2, 129.9, 125.5 (C-4"), 130.4 (C-5), 122.0 (C-4'"), 131.5 (C-3"), 124.0 (C-2"), 129.9 (C-2'"), 131.0 (C-3'"), 125.9 (C-7), 125.0 (C-6), 117.6 (C-8), 90.0 (C-1').

Anal. Calcd. for $C_{22}H_{14}N_2OBr_2$: C, 54.78; K, 2.93; N, 5.81. Found: C, 54.62; H, 2.88; N, 5.75.

2-(*p*-Methylbenzoylmethylene)-3-(*p*-methylphenyl)-6,7-dimethyl-1*H*-quinoxaline **2e**.

This compound had ms: EI m/z (relative abundance) 380 (M^+, 15), 261 (50), 119 (100); ^{13}C nmr δ 179.4 (C2'), 158.3, 147.6, 137.0, 135.9, 131.0, 129.9, 141.8 (C-4"), 129.0 (C-5), 140.3 (C-4'"), 129.0 (C-3"), 128.5 (C-2"), 128.2 (C-2'"), 127.3 (C-3'"), 134.4 (C-7), 130.2 (C-6), 118.8 (C-8), 90.5 (C-1'), 25.2, 25.0, 23.5 and 23.0 (CH_3-).

Anal. Calcd. for $C_{26}H_{24}N_2O$: C, 82.07; H, 6.36; N, 7.36. Found: C, 81.67; H, 6.22; N, 7.52.

2-(*p*-Chlorobenzoylmethylene)-3-(*p*-chlorophenyl)-6,7-dimethyl-1*H*-quinoxaline **2f**.

This compound had ms: EI m/z (relative abundance) 420 (M^+, 64), 281 (36), 139 (100); ^{13}C nmr δ 180.9 (C2'), 161.1, 145.3, 136.7, 136.5, 132.1, 131.3, 139.2 (C-4"), 130.1 (C-5), 135.3 (C-4'"), 129.8 (C-3"), 130.9 (C-2"), 127.8 (C-2'"), 128.4 (C-3'"), 134.4 (C-7), 130.2 (C-6), 117.9 (C-8), 90.5 (C-1'), 25.5 and 23.5 (CH_3-).

Anal. Calcd. for $C_{24}H_{18}N_2OCl_2$: C, 68.42; H, 4.31; N, 6.65. Found: C, 67.98; H, 4.37; N, 6.72.

2-(*p*-Bromobenzoylmethylene)-3-(*p*-bromophenyl)-6,7-dimethyl-1*H*-quinoxalines **2g**.

This compound had ms: EI m/z (relative abundance) 508 (M+, 98), 325 (28), 183 (100); ^{13}C nmr δ 181.9 (C2'), 162.5, 148.9, 136.8, 136.9, 131.9, 129.0, 125.3 (C-4"), 130.1 (C-5), 122.1 (C-4'"), 131.3 (C-3"), 124.8 (C-2"), 129.9 (C-2'"), 131.1 (C-3'"), 134.5 (C-7), 130.0 (C-6), 118.0 (C-8), 91.0 (C-1'), 24.5 and 24.1 (CH_3-).

Anal. Calcd. for $C_{24}H_{18}N_2OBr_2$: C, 56.49; H, 3.56; N, 5.49. Found: C, 57.02; H, 3.50; N, 5.63.

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REFERENCES AND NOTES

[1] E. Rodd, Chemistry of Carbon Compounds, A Modern Comprehensive Treatise, Vol **4B**, 1346.

[2] V. D. Orlov, N. P. Vorobeva, N. N. Demenkova, V. S. Chesnovski, and F. G. Yaremenko, *Khim. Geterosikl. Soedin.*, 328 (1988).

[3] N. N. Kolos, B. Insuasty, J. Quiroga, and V. D. Orlov, *Khim. Geterosikl. Soedin.*, 1127 (1986).

[4] V. D. Orlov, B. Insuasty, and N. N. Kolos, *Khim. Geterosikl. Soedin.*, 830 (1987).

[5] J. V. Greenhill, *Chem. Soc. Rev.*, **6**, 227 (1977).