Synthesis and Structural Elucidation of the Acetylation Reaction's Product(s) of the 2(1H)-Quinoxalinones Derived from L-Ascorbic Acid.

X-Ray Molecular Structure of

3-(N-acetyl-2-naphthylhydrazono)-2,3-dihydro-2-acetoxylfuro[2,3-b]quinoxaline [1]

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Dedicated to Professor Dr. Hans Zimmer on the occasion of his 71st birthday

Z. Naturforsch. **47b**, 861–868 (1992); received August 13, 1991

Quinoxalin-2(1H)-one, 3-(Pyrazol-3-yl)quinoxalin-2(1H)-one, Furo[2,3-b]quinoxaline,
Crystal Structure, Tautomerism

Acetylation reaction's product(s) of 3-[L-threo-2,3,4-trihydroxy-1-(2-naphthylhydrazono)-butyl]quinoxalin-2(1H)-one (**2b**) were found to be dependent on the reaction condition. While the tri-O-acetyl (**3b**) was isolated in high yield from **2b** under the action of acetic anhydride/pyridine mixture, compounds **4b** and **5b** as well as trace of **3b** were obtained when **2b** was heated in acetic anhydride. On the other hand, 3-[1-(2-naphthylhydrazono)-glyoxal-1-yl]quinoxalin-2(1H)-one (**7**) underwent ring closure and afforded the condensed tricyclic compound **8** under the action of acetic anhydride/pyridine mixture.

Introduction

The chemical versatility of L-ascorbic acid (**1**) and its synthetic applicability are of considerable interest [2–5]. The multifunctional character of this molecule confers an intriguing synthetic potential, which has prompted us to explore some of its chemistry [6–8]. Recently, we reported on the

proof of structure of the reaction product from dehydroascorbic acid, *o*-phenylenediamine and phenylhydrazine as 3-[L-threo-2,3,4-trihydroxy-1-(phenylhydrazono)butyl]quinoxalin-2(1H)-one (**2a**) [1]. Its structure was confirmed by successful

transformation to its tri-O-acetyl analog **3a** under the action of acetic anhydride-pyridine mixture. Heating **2a** in ethanol led to 3-[5-(acetoxymethyl)-1-phenylpyrazol-3-yl]quinoxalin-2(1H)-one (**4a**). As a continuation of our interest in the chemistry of quinoxalinone ring system [6–10], we report herein on the details of our investigation toward the effect of the acetylation condition on **2b** and 3-[1-(2-naphthylhydrazono)-glyoxal-1-yl]quinoxalin-2(1H)-one (**7**).

Results and Discussion

Compound **2b** (Ar = 2-C₁₀H₇) needed for this present work was prepared following the previously established method. Its 1D ¹H NMR spectra re-

a) Ar = C₆H₅
b) Ar = 2-C₁₀H₇

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Fig. 1. Partial COSY spectrum of **2b** showing the sugar resonances.

vealed that in $(\text{CD}_3)_2\text{SO}$ solution it exists as a tautomeric mixture of the hydrazone imine form A and the diazenyl enamine form B. The assignment of the protons resonances to specific tautomeric form was based on integrals, characteristic chemical shifts and deuterium-exchange experiment. Also, largely clarified by means of 2D ^1H - ^1H homonuclear-correlated experiment (COSY-SMX) (Fig. 1). The δ 3.44 multiplet gives a strong cross-peak to the multiplet at δ 3.61. Both multiplets (H-4'A, H-4''A, H-4'B and H-4''B) also correlate with the multiplets at δ 3.83 (H-3'A), 3.92 (H-3'B), 4.52 (OH at C-4', D_2O exchangeable) and 4.76 (H-2'A). The multiplet at δ 3.83 (H-3'A) connects to the multiplets at δ 4.52 (D_2O exchangeable) and 4.76 while the multiplet at δ 3.92 (H-3'B) shows a cross-peak to the δ 5.22 doublet (D_2O exchangeable) and the δ 5.33 broad singlet. Thus δ 4.52, 4.76, 4.89, 5.22 and 5.33 resonances were assigned to OHs at C-4'A & B and C-3'A (overlapped), H-2'A, OH at C-2'A, OH at C-3'B and H-2'B pro-

tons of the sugar part. The OH at C-2'B was detected at δ 6.12 and showed correlation to the δ 5.33 (H-2'B). Consideration of the remainder of the proton spectrum reveals a multiplet at δ 7.25–7.91 which arises from the eleven aromatic protons. The low-field exchangeable singlets at δ 10.42, 10.93, 12.34 and 12.59 were assigned to N–NH, N(4)–H, N(1)–HB and N(1)–HA respectively.

Treatment of **2b** with acetic anhydride-pyridine mixture afforded the triacetoxo analog **3b** in high yield (Scheme 1). Its structure again was supported by spectral data and microanalytical results. ^1H NMR spectrum (250 MHz) showed the three different acetyl groups as two singlets at δ_{H} 2.20 and 2.06 in 1:2 ratio and the ^{13}C NMR (75.5 MHz) showed the resonances of these acetate methyls at δ_{C} 21.23, 21.05 and 20.89.

On the other hand, heating **2b** in acetic anhydride for 5 min led to the formation of **4b** and **5b** in $\sim$ 3:1 ratio as well as trace of **3b** (Scheme 1).

Scheme 1

They were easily separated by flash column chromatography using ethyl acetate as an eluent. Their structure assignments were based on elemental analyses and spectral data. ¹H NMR spectrum of **4b** exhibited three singlets (δ_{H} 12.23, 5.26, 2.13) with relative intensities 1:2:3, caused by NH (D₂O exchangeable), CH₂O and CH₃ groups respectively. The aromatic protons gave multiplet centered at 7.58 ppm. Chemical ionization mass spectrum of **4b** showed $M^+ + 1$ at m/z 411. The IR spectrum of **4b** exhibits intense bands at 1744 and 1673 cm⁻¹ which were assigned to the $\nu(\text{OC}=\text{O})$ and $\nu(\text{NC}=\text{O})$ modes; the $\nu(\text{N}-\text{H})$ band was found at 3686 cm⁻¹ (a low-intensity band). Compound **5b** showed two different acetyl groups responsible for signals at δ_{H} 2.35, 2.12 (2s). The methylene and aromatic protons caused singlet and multiplet at δ 5.24 and 7.78 respectively. Its mass spectrum (EI) showed the molecular ion at m/z 452 (RI = 1%) and the base peak at m/z 42. The wave number values $\nu(\text{OC}=\text{O})$ 1770 and 1746 cm⁻¹ and the absence of $\nu(\text{NC}=\text{O})$ band is in accord with the proposed O-acetyl structure **5b** rather than the N-acetyl **6**.

Periodate oxidation of **2b** carried out by treatment of its suspension in water, with sodium metaperiodate, gave 3-[1-(2-naphthylhydrazono)-glyoxal-1-yl]quinoxalin-2(1H)-one (**7**) (Scheme 2). ¹H NMR spectrum measured in hexadeuteriodimethyl sulfoxide showed that compound **7** exists only in one tautomeric form.

Scheme 2

In order to examine the reactivity of **7** under acetylative condition we carried out an experiment involving the reaction of **7** with acetic anhydride/pyridine mixture and worked it up in the usual manner (see experimental section). A yellow crystalline solid of m.p. 224 °C was isolated. An empirical formula of C₂₄H₁₈N₄O₄ from combustion analysis and a molecular ion at m/z 426 (RI = 6%) estimated from its mass spectrum, indicated the acetylation of two sites of **7**.

1D ¹H and ¹³C NMR spectroscopy were inconclusive in elucidating the structure (vide infra) and the product was finally identified unambiguously as **8** by X-ray crystallography. A perspective view of **8** is presented in Fig. 2. Final atomic coordinates are given in Table I and bond distances and bond angles in Tables II and III, respectively.

With its structure in hand, the formation of **8** can be visualized easily since pyridine will be able to remove the proton from N-1 thereby facilitating the attack of the cyclic amide oxygen on the aldehyde electrophilic carbon followed by acetylation of its oxygen as shown below.

Table I. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{C}_{24}\text{H}_{18}\text{N}_4\text{O}_4$.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^+
O(1)	−3086(∗)	4184(1)	1806(∗)	53(1)
C(2)	−1350(7)	4217(2)	1277(3)	46(1)
C(3)	−1095(7)	3604(2)	920(3)	44(1)
C(3a)	−2516(7)	3232(2)	1370(3)	43(1)
N(4)	−2798(7)	2665(1)	1359(3)	50(1)
C(4a)	−4369(7)	2467(2)	1845(3)	49(1)
C(5)	−4812(8)	1861(2)	1872(3)	61(2)
C(6)	−6429(9)	1660(2)	2316(3)	69(2)
C(7)	−7653(9)	2043(2)	2756(4)	68(2)
C(8)	−7237(8)	2633(2)	2750(3)	62(2)
C(8a)	−5571(7)	2860(2)	2307(3)	49(1)
N(9)	−5163(6)	3454(1)	2335(3)	53(1)
C(9a)	−3671(7)	3608(2)	1880(3)	47(1)
O(10)	688(6)	4377(1)	1840(2)	51(1)
C(11)	929(8)	4968(2)	2038(3)	55(1)
O(11)	−501(7)	5311(1)	1748(3)	75(1)
C(12)	3120(8)	5084(2)	2618(4)	71(2)
N(13)	48(7)	3387(1)	366(3)	46(1)
N(14)	1341(7)	3721(1)	−93(3)	49(1)
C(15)	2741(8)	3410(2)	−564(3)	52(1)
O(15)	3970(7)	3684(1)	−962(3)	77(1)
C(16)	2655(10)	2759(2)	−538(4)	62(2)
C(1′)	2780(7)	4715(2)	143(3)	48(1)
C(2′)	1087(7)	4348(2)	−222(3)	46(1)
C(3′)	−918(8)	4568(2)	−751(3)	54(1)
C(4′)	−1151(8)	5158(2)	−878(3)	55(1)
C(4a′)	558(7)	5555(2)	−507(3)	49(1)
C(5′)	350(9)	6174(2)	−617(3)	60(2)
C(6′)	2059(10)	6535(2)	−244(3)	69(2)
C(7′)	4042(10)	6315(2)	253(4)	67(2)
C(8′)	4318(9)	5725(2)	371(3)	60(2)
C(8a′)	2573(7)	5331(2)	6(3)	46(1)

* Parameters constrained to define the origin in the monoclinic space group Cc (No. 9); + Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table II. Bond distances (Å) for $\text{C}_{24}\text{H}_{18}\text{N}_4\text{O}_4$.

O(1)–C(2)	1.437(5)
O(1)–C(9a)	1.370(4)
C(2)–C(3)	1.518(5)
C(2)–O(10)	1.412(5)
C(3)–C(3a)	1.465(6)
C(3)–N(13)	1.284(6)
C(3a)–N(4)	1.304(5)
C(3a)–C(9a)	1.424(6)
N(4)–C(4a)	1.383(6)
C(4a)–C(5)	1.408(6)
C(4a)–C(8a)	1.419(6)
C(5)–C(6)	1.366(8)
C(6)–C(7)	1.394(8)
C(7)–C(8)	1.370(7)
C(8)–C(8a)	1.408(7)
C(8a)–N(9)	1.376(5)
N(9)–C(9a)	1.283(6)
O(10)–C(11)	1.382(5)
C(11)–O(11)	1.189(5)
C(11)–C(12)	1.473(6)
N(13)–N(14)	1.370(6)
N(14)–C(15)	1.398(6)
N(14)–C(2′)	1.448(5)
C(15)–O(15)	1.214(6)
C(15)–C(16)	1.486(6)
C(1′)–C(2′)	1.359(6)
C(1′)–C(8a′)	1.422(5)
C(2′)–C(3′)	1.416(6)
C(3′)–C(4′)	1.364(6)
C(4′)–C(4a′)	1.410(6)
C(4a′)–C(5′)	1.424(6)
C(4a′)–C(8a′)	1.415(6)
C(5′)–C(6′)	1.361(7)
C(6′)–C(7′)	1.387(7)
C(7′)–C(8′)	1.363(7)
C(8′)–C(8a′)	1.418(6)
C(2)–H(2)	0.997(31)
C(5)–H(5)	0.971(52)
C(6)–H(6)	0.932(43)
C(7)–H(7)	0.917(44)
C(8)–H(8)	0.973(51)
C(12)–H(12a)	0.960
C(12)–H(12b)	0.960
C(12)–H(12c)	0.960
C(16)–H(16a)	0.938(51)
C(16)–H(16b)	1.004(53)
C(16)–H(16c)	0.930(56)
C(1′)–H(1′)	0.955(37)
C(3′)–H(3′)	0.972(44)
C(4′)–H(4′)	0.977(40)
C(5′)–H(5′)	0.912(44)
C(6′)–H(6′)	0.972(47)
C(7′)–H(7′)	0.943(48)
C(8′)–H(8′)	0.903(41)

Table III. Bond angles (°) for C₂₄H₁₈N₄O₄.

C(2)–O(1)–C(9a)	108.8(3)	C(5')–C(4a')–C(8a')	118.1(4)
O(1)–C(2)–C(3)	106.6(3)	C(4a')–C(5')–C(6')	120.5(4)
O(1)–C(2)–O(10)	108.5(3)	C(5')–C(6')–C(7')	121.3(4)
C(3)–C(2)–O(10)	108.7(3)	C(6')–C(7')–C(8')	120.1(5)
C(2)–C(3)–C(3a)	105.0(4)	C(7')–C(8')–C(8a')	120.6(4)
C(2)–C(3)–N(13)	133.9(4)	C(1')–C(8a')–C(4a')	118.7(3)
C(3a)–C(3)–N(13)	121.1(3)	C(1')–C(8a')–C(8')	122.0(4)
C(3)–C(3a)–N(4)	131.0(4)	C(4a')–C(8a')–C(8')	119.3(3)
C(3)–C(3a)–C(9a)	107.1(3)	O(1)–C(2)–H(2)	107.0(19)
N(4)–C(3a)–C(9a)	121.9(4)	H(2)–C(2)–C(3)	115.6(19)
C(3a)–N(4)–C(4a)	114.7(4)	H(2)–C(2)–O(10)	110.0(17)
N(4)–C(4a)–C(5)	119.2(4)	C(4a)–C(5)–H(5)	115.0(28)
N(4)–C(4a)–C(8a)	121.5(3)	H(5)–C(5)–C(6)	124.9(28)
C(5)–C(4a)–C(8a)	119.2(4)	C(5)–C(6)–H(6)	120.7(26)
C(4a)–C(5)–C(6)	120.1(5)	H(6)–C(6)–C(7)	118.1(26)
C(5)–C(6)–C(7)	121.2(5)	C(6)–C(7)–H(7)	121.7(24)
C(6)–C(7)–C(8)	119.9(5)	H(7)–C(7)–C(8)	118.3(24)
C(7)–C(8)–C(8a)	120.8(5)	C(7)–C(8)–H(8)	123.8(31)
C(4a)–C(8a)–C(8)	118.7(4)	H(8)–C(8)–C(8a)	115.3(31)
C(4a)–C(8a)–N(9)	122.2(4)	C(11)–C(12)–H(12a)	109.5(2)
C(8)–C(8a)–N(9)	119.1(4)	C(11)–C(12)–H(12b)	109.5(3)
C(8a)–N(9)–C(9a)	113.1(4)	H(12a)–C(13)–H(12b)	109.5(1)
O(1)–C(9a)–C(3a)	111.9(4)	C(11)–C(12)–H(12c)	109.3(3)
O(1)–C(9a)–N(9)	121.6(4)	H(12a)–C(12)–H(12c)	109.5(1)
C(3a)–C(9a)–N(9)	126.4(4)	H(12b)–C(12)–H(12c)	109.5(1)
C(2)–O(10)–C(11)	115.4(3)	C(15)–C(16)–H(16a)	108.1(28)
O(10)–C(11)–O(11)	121.4(4)	C(15)–C(16)–H(16b)	114.7(27)
O(10)–C(11)–C(12)	110.7(4)	H(16a)–C(16)–H(16b)	99.6(40)
O(11)–C(11)–C(12)	128.0(4)	C(15)–C(16)–H(16c)	109.0(31)
C(3)–N(13)–N(14)	123.1(3)	H(16a)–C(16)–H(16c)	117.7(42)
N(13)–N(14)–C(15)	115.8(3)	H(16b)–C(16)–H(16c)	107.7(42)
N(13)–N(14)–C(2')	124.2(4)	H(1')–C(1')–C(2')	119.3(22)
C(15)–N(14)–C(2')	119.3(4)	H(1')–C(1')–C(8a')	120.1(22)
N(14)–C(15)–O(15)	118.6(4)	C(2')–C(3')–H(3')	115.7(25)
N(14)–C(15)–C(16)	117.7(4)	H(3')–C(3')–C(4')	125.3(25)
O(15)–C(15)–C(16)	123.7(5)	C(3')–C(4')–H(4')	121.6(23)
C(2')–C(1')–C(8a')	120.6(4)	H(4')–C(4')–C(4a')	116.5(22)
N(14)–C(2')–C(1')	120.0(4)	C(4a')–C(5')–H(5')	116.0(29)
N(14)–C(2')–C(3')	119.0(4)	H(5')–C(5')–C(6')	123.4(29)
C(1')–C(2')–C(3')	121.0(4)	C(5')–C(6')–H(6')	124.9(23)
C(2')–C(3')–C(4')	119.0(4)	H(6')–C(6')–C(7')	113.7(23)
C(3')–C(4')–C(4a')	121.9(4)	C(6')–C(7')–H(7')	121.2(32)
C(4')–C(4a')–C(5')	123.1(4)	H(7')–C(7')–C(8')	118.6(31)
C(4')–C(4a')–C(8a')	118.8(3)	C(7')–C(8')–H(8')	118.8(25)
		H(8')–C(8')–C(8a')	120.4(25)

Fig. 2. Perspective drawing of compound **8** with atom-labelling scheme.

Table IV. Structure determination summary for $C_{24}H_{18}N_4O_4$.*Crystal data*

Formula	$C_{24}H_{18}N_4O_4$
Color and habit	pale yellow prisms
Size (mm)	$0.12 \times 0.30 \times 0.38$
Crystal system	monoclinic
Space group	Cc (No. 9)
Unit cell dimensions	$a = 6.0392(6)$
(a, b, c in Å)	$b = 22.808(3)$
(angles in °)	$c = 15.232(2)$
Volume (Å ³)	$\beta = 100.617(9)$
Z (formulae/cell)	2062.2(4)
Formula weight	4
Density, calc. (g/cc)	426.46
Absorption coeff. (cm ⁻¹)	1.37
F(000) (e ⁻)	0.90
	888

Data collection

Diffractometer	Siemens R 3 m/V
Radiation	MoK α ($\lambda = 0.71073$ Å)
Monochromator	highly oriented graphite crystal
Temperature (K)	294
2 θ Range (deg.)	4.0 to 55.0
h, k, l Limits	$-7 \rightarrow 7, 0 \rightarrow 29, 0 \rightarrow 19$ plus Friedels
Scan type	$2\theta - \theta$
Scan speed (deg./min)	variable; 4.0 to 8.0
Scan range (deg.)	0.8 on either side of K α 2
Background measurement	stationary crystal and counter at beginning and end of scan; total background time to scan time ratio of 0.5
Standard reflections	3 measured every 37
Reflections collected	5039 total; 4745 independent; $R(\text{int}) = 0.0159$
Reflections observed	3008; $F > 3 \cdot \sigma(F)$
Absorption correction	N/A
Min./max. transmission	N/A

Solution and refinement

System used	Siemens SHELXTL PLUS (Micro VAX II)
Solution	direct methods (XS: TREF)
Refinement method	Full-Matrix Least-Squares (XLS)
Absolute configuration	N/A
Extinction correction	$X = 0.0006(1)$
Final residuals	$R(F) = 0.0501$
Goodness-of-fit	$S = 0.96$
Max. and mean $ \text{shift}/\text{ESD} $	$wR(F) = 0.0591$
Number of variables	0.001 and 0.000
Data-to-parameter ratio	348
Max./min. excursions	8.6:1
	0.29 and $-0.32 \text{ e}^-/\text{\AA}^3$

The quantity minimized was $\Sigma w(F_o - F_c)^2$. $F^* = F_c[1.0 + 0.002 X F_c^2 / \sin(2\theta)]^{-1/4}$; $R(F) = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$; $wR(F) = [\Sigma(w \cdot ||F_o| - |F_c||^2) / \Sigma w \cdot |F_o|^2]^{1/2}$; $w = [\sigma^2(F) + |g|(F^2)]^{-1}$; $g = 0.001504$; $S = [\Sigma(w \cdot ||F_o| - |F_c||^2) / (M - N)]^{1/2}$ where M is the number of observed reflections, and N is the number of parameters refined.

Experimental

Melting points were determined with a Mel Temp apparatus and are uncorrected. NMR spectra were recorded on a Bruker AC-250 MHz spectrometer. Chemical shifts are expressed in δ (ppm) relative to tetramethylsilane as internal standard.

Elemental analyses were performed at M-H-W Laboratories, Phoenix, Arizona. Silica gel 60 (Merck) was used for column chromatography and ethyl acetate as an eluent. The reported yields refer to pure isolated materials. Crystal structure determination was done on a Nicolet R 3 M four-circle diffractometer.

3-[L-threo-2,3,4-Trihydroxy-1-(2-naphthylhydrazono)butyl]quinoxalin-2(1H)-one (2b)

A suspension of 4.4 g (0.025 mol) L-ascorbic acid and 2.7 g (0.025 mol) *p*-benzoquinone in 40 ml ethanol was stirred for 1 h at room temperature. The resulting homogenous redish orange solution was treated with a solution of 2.7 g (0.025 mol) *o*-phenylenediamine in 25 ml ethanol and 125 ml water and then heated until boiling. The reaction mixture was then treated with a solution of 2.9 g (0.025 mol) 2-naphthylhydrazine hydrochloride and 2.07 g (0.025 mol) sodium acetate in 50 ml ethanol and 25 ml water. The mixture was heated under reflux for 20 min whereby a redish orange crystalline product separated out; yield 7.20 g (71%), m.p. 290–292 °C (decomp.). ¹H NMR [(CD₃)₂SO]: δ = 12.59 (s, 0.7H), 12.34 (s, 0.3H), 10.93 (s, 0.3H), 10.42 (s, 0.7H), 7.91–7.25 (m, 11H), 6.12 (d, 0.3H), 5.33 (t, 0.3H), 5.22 (d, 0.3H), 4.89 (d, 0.7H), 4.76 (m, 0.6H), 4.52 (m, 1.7H), 3.92, 3.83 (2m, 1H), 3.61, 3.44 (2m, 2H).

C₂₂H₂₀N₄O₄ (404.41)

Calcd C 65.33 H 4.99,
Found C 65.12 H 4.98.

3-[L-threo-2,3,4-Tri-O-acetoxy-1-(2-naphthylhydrazono)butyl]quinoxaline-2(1H)-one (3b)

A solution of 1.01 g (0.0025 mol) **2b** in 12 ml pyridine was treated with 2 ml (0.021 mol) acetic anhydride and the mixture was kept at room temperature for 3 days. The reaction mixture was then poured onto crushed ice and the title product that separated out was filtered off, washed repeatedly with water and dried. It was recrystallized from chloroform-methanol in the cold; yield 1.29 g (97%), m.p. 163 °C. ¹H NMR (CDCl₃): δ = 14.67 (s, 1H), 12.34 (s, 1H), 7.84–7.11 (m, 11H), 6.10 (m, 1H), 4.58 (2dd, 2H), 2.20 (s, 3H), 2.06 (s, 6H). ¹³C NMR (CDCl₃): δ = 170.92, 170.74, 170.63, 155.98, 148.69, 141.05, 134.34, 131.26, 130.96, 130.63, 130.33, 129.56, 129.52, 128.60, 127.88, 127.08, 126.75, 124.68, 124.20, 115.69, 115.61, 109.87, 72.02, 71.90, 63.51, 21.22, 21.05, 20.89.

C₂₈H₂₆N₄O₇ (530.52)

Calcd C 63.39 H 4.94,
Found C 63.41 H 5.03.

Action of boiling acetic anhydride on 2b

A solution of 0.2 g (0.0005 mol) **2b** in 2 ml (0.021 mol) acetic anhydride was heated under reflux for 10 min. The reaction mixture was cooled and poured onto crushed ice. The product that separated out was filtered off, washed with water

and dried. Column chromatography (silica gel, ethyl acetate) gave 0.05 g (22%) **4b** as colorless solid, m.p. 252 °C. ¹H NMR (CDCl₃): δ = 12.23 (s, 1H), 7.60 (m, 11H), 5.26 (s, 2H), 2.13 (s, 3H). IR (CHCl₃): ν 3686, 1744, 1673. MS (CI): *m/z* = 411, 367, 338, 309, 190, 105, 85, 69.

C₂₄H₁₈N₄O₃ (410.42)

Calcd C 70.23 H 4.42,
Found C 70.39 H 4.52.

0.016 g (7%) **5b** as colorless solid, m.p. 160 °C. ¹H NMR (CDCl₃): δ = 7.78 (m, 11H), 5.24 (s, 2H), 2.35 (s, 3H), 2.12 (s, 3H). IR (CHCl₃): ν 1770, 1746. MS (EI): *m/z* = 452 (RI = 1%), 411 (1), 410 (4), 382 (2), 339 (2), 42 (100).

C₂₆H₂₀N₄O₄ (452.45)

Calcd C 69.01 H 4.46,
Found C 68.86 H 4.52.

3-[1-(2-Naphthylhydrazono)-glyoxal-1-yl]-quinoxalin-2(1H)-one (7)

A suspension of 5 g (0.0124 mol) **2b** in 60 ml water was treated with a solution of 6.62 g (0.0309 mol) sodium metaperiodate in 40 ml water. The reaction mixture was stirred at room temperature for 1 h and then left overnight in the dark. The product was filtered off, washed with water and crystallized from methanol as orange crystals; yield 4.06 g (95.5%), m.p. 255 °C. ¹H NMR [(CD₃)₂SO]: δ = 12.88 (s, 1H), 11.43 (s, 1H), 9.67 (s, 1H), 7.67 (m, 11H). IR (KBr): ν 3448, 3265, 1670, 1653.

C₂₀H₁₄N₄O₂ (342.34)

Calcd C 70.16 H 4.12,
Found C 70.25 H 4.10.

3-(N-Acetyl-2-naphthylhydrazono)-2,3-dihydro-2-acetoxyfuro[2,3-b]quinoxaline (8)

A solution of 0.3 g (0.0009 mol) **7** in 3 ml pyridine was treated with 1 ml (0.011 mol) acetic anhydride and the mixture was kept at room temperature for 2 days. The reaction mixture was then poured onto crushed ice and the product that separated out was filtered off, washed repeatedly with water and dried. Column chromatography (silica gel, ethyl acetate) gave 0.18 g (47.4%) **8** as pale yellow crystals, m.p. 224 °C. ¹H NMR (CDCl₃): δ = 7.69 (m, 11H), 6.13 (s, 1H), 2.81 (s, 3H), 1.81 (s, 3H). ¹³C NMR (CDCl₃): δ = 174.22, 167.33, 160.25, 141.54, 141.17, 140.17, 138.26, 135.479, 133.50, 133.20, 131.38, 130.08, 129.99, 128.14, 128.053, 127.97, 127.89, 127.5, 125.23, 89.72,

22.49, 20.38. MS (EI): m/z = 426 (RI = 6%), 384 (18), 268 (12), 143 (13), 127 (26), 115 (18), 43 (100).

$C_{24}H_{18}N_4O_4$ (426.42)

Calcd C 67.60 H 4.25,

Found C 67.73 H 4.19.

Structure determination summary for compound **8** ($C_{24}H_{18}N_4O_4$) (see Table IV).

A. A. is grateful to Professor M. Mokbel Abdel Rahman for his continuous encouragement. Thanks are due Mrs. Elaine Seliskar for the neat and efficient preparation of this manuscript.

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