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Note

Periodate-oxidation products of 3-substituted 2-quinoxalinones: preparation of glyoxalylquinoxalinones*

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The structural assignment of the reaction product[2] of L-*threo*-2,3-hexodiulosono-1,4-lactone with *o*-phenylenediamine and phenylhydrazine to be the hydrated, anhydro structure 2,2′-anhydro-[2-hydroxy-3-(1-phenylhydrazono-L-*threo*-2,3,4-trihydroxybutyl)quinoxaline] (**1**) was based on the formation of a di-*O*-acetyl derivative[2], whereas its periodate-oxidation product[3,4] indicated its presence as 3-[(1-phenylhydrazono)-L-*threo*-2,3,4-trihydroxybutyl]-2-quinoxalinone (**2**) having an acyclic side-chain. In a previous report[4], we extended this reaction by using a variety of arylhydrazines, and in this Note, we describe their periodate-oxidation products, and confirm their structures, which agree with those anticipated from **2** (the infrared data also agree with **2** rather than **1**). In addition, this study provides a simple route to glyoxalylquinoxalinones of great potentiality as precursors to other heterocyclic compounds.

When **2–6** were treated with sodium metaperiodate, either in alcoholic solution, or as a suspension in water, they afforded the corresponding aldehydes, 3-[(1-arylhydrazono)glyoxal-1-yl]-2-quinoxalinones (**7–11**). This assignment was based on the elemental analyses, as well as the mass spectrometry. Their infrared (i.r.) spectra showed two absorption bands, at 1700–1680 cm^{-1} (due to the aldehydic group) and 1660–1650 cm^{-1} (due to the amide).

The mass spectrum of 3-[1-*p*-tolylhydrazono)glyoxal-1-yl]-2-quinoxalinone (**7**) showed a molecular-ion peak at *m/e* 306, which was followed by a series of peaks due to the loss of CH_3 and CHO at *m/e* 291 (confirmed by the presence of a metastable-ion peak) and 277, which lose CHO and CH_3, respectively, to give an ion at *m/e* 262. The ion at *m/e* 277 undergoes fission of the heterocyclic ring to give the ion at *m/e* 172 as the base peak. Fission of the side chain at C-3 occurred, to give an ion at *m/e* 145 corresponding to the heterocyclic ring. In addition, there were peaks at *m/e* 107, 91, 77, and 65, all of which agreed with the assigned structure.

Reaction of **7** with *N*,*N*′-diphenyl-1,2-ethanediamine gave 3-[2-(1,3-diphenyl-

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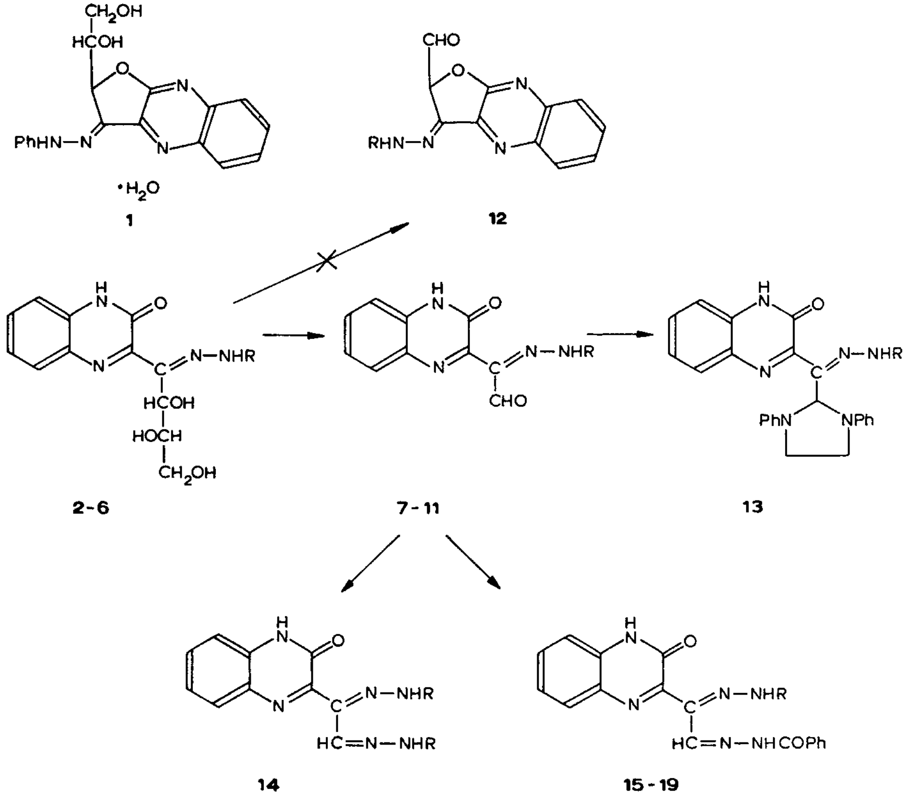
*Heterocycles from Carbohydrate Precursors. Part VII. For Part VI, see ref. 4. For Part V, see ref. 1.



R = Ph, C_6H_4Me-*p*, C_6H_4Cl-*p*, C_6H_4Br-*p*, C_6H_4I-*p*, and $C_6H_4NO_2$-*p*

imidazolidin-2-yl)-1-(*p*-tolylhydrazono)glyoxal-1-yl]-2-quinoxalinone (**13**), which showed the amide band at 1640 cm^{-1} in its i.r. spectrum, whereas the aldehydic group in its precursor **7** had disappeared. When **10** was treated with (*p*-iodophenyl)-hydrazine, it gave the corresponding bis(arylhydrazone) (**14**), which also lacked an aldehydic group (i.r. spectrum). Treatment of the aldehydes **7–11** with benzoylhydrazine gave the corresponding, mixed bishydrazones, the 3-[1-(arylhydrazono)-2-(benzoylhydrazono)glyoxal-1-yl]-2-quinoxalinones (**15–19**).

From these results, it may be concluded that the periodate oxidation of **2–6** gives **7–11** (not **12**). The isolation of **7** indicates the formulation of supposed **1** in the partially acyclic structure **2**. The periodate-oxidation products resulting by this simple route are important starting-materials for the synthesis of a variety of heterocycles.

EXPERIMENTAL

General methods. — Melting points were determined with a Kofler-block apparatus and are uncorrected. I.r. spectra were recorded with a Unicam SP200 spectrometer. Mass spectra were recorded with an A.E.I. MS902 instrument; in-

TABLE I

MICROANALYTICAL AND SPECTRAL DATA FOR 3-(1-ARYLHYDRAZONO-GLYOXAL-1-YL)-2-QUINOXALINONES

Compound No.	*R*	*Yield (%)*	*M.p. (degrees)*	*Molecular formula*	*Calculated (%)*			*Found (%)*			ν_{max}^{Nujol} *(cm^{-1})*
					C	*H*	*N*	*C*	*H*	*N*	
7	C_6H_4Me-*p*	85	240–242	$C_{17}H_{14}N_4O_2$	66.7	4.6	18.3	66.4	4.8	18.1	1650 1680
8	C_6H_4Cl-*p*	88	264–265	$C_{16}H_{11}ClN_4O_2$	58.8	3.4	17.1	58.8	3.6	16.9	1660 1700
9	C_6H_4Br-*p*	96	280–282	$C_{16}H_{11}BrN_4O_2$	51.8	3.0	15.1	52.0	2.9	15.5	1660 1700
10	C_6H_4I-*p*	90	269–270	$C_{16}H_{11}IN_4O_2$	45.9	2.7	13.4	45.6	2.4	13.0	1660 1680
11	$C_6H_4NO_2$-*p*	89	284–286	$C_{16}H_{11}N_5O_4$	57.0	3.3	20.8	57.1	3.5	21.0	1660 1700

TABLE II

MICROANALYTICAL AND SPECTRAL DATA FOR COMPOUNDS **13–19**

Compound No.	*R*	*Yield (%)*	*M.p. (degrees)*	*Molecular formula*	*Calculated (%)*			*Found (%)*			ν_{max}^{Nujol} *(cm^{-1})*
					C	*H*	*N*	*C*	*H*	*N*	
13	C_6H_4Me-*p*	75	208–210	$C_{20}H_{26}N_6O$	65.6	7.2	22.9	65.4	7.5	23.1	1640
14	C_6H_4I-*p*	80	270–271	$C_{22}H_{16}I_2N_6O$	40.6	2.5	12.9	40.4	2.3	13.1	1660
15	C_6H_4Me-*p*	88	258–260	$C_{24}H_{20}N_6O_2$	67.9	4.8	19.8	68.2	4.9	20.1	1645, 1660
16	C_6H_4Cl-*p*	90	262–264	$C_{23}H_{17}ClN_6O_2$	62.1	3.9	18.9	62.5	4.0	18.6	1650(sh), 1660
17	C_6H_4Br-*p*	90	262–264	$C_{23}H_{17}BrN_6O_2$	56.5	3.5	17.2	56.2	3.3	17.5	1650(sh), 1660
18	C_6H_4I-*p*	85	255–258	$C_{23}H_{17}IN_6O_2$	51.5	3.2	15.7	51.4	3.0	15.4	1650(sh), 1660
19	$C_6H_4NO_2$-*p*	80	273–275	$C_{23}H_{17}N_7O_4$	59.6	3.9	22.1	60.0	4.1	21.9	1645, 1660

tensities are given in parentheses, as percentages of the base peak. Microanalyses were performed in the Chemistry Department, Faculty of Science, Cairo University, Cairo, Egypt.

3-[1-(Arylhydrazono)glyoxal-1-yl]-2-quinoxalinones (**7–11**). — A suspension of **2–6** (0.01 mole) in water (150 ml) was treated with a solution of sodium metaperiodate (0.03 mole) in water (50 ml). The mixture was stirred for 4 h at room temperature and then kept overnight in the dark. The crystals were filtered off, washed with water, and recrystallized from butanol in orange needles (see Table I). Mass-spectral data for compound **7**: *m/e* 308 (2, $M^{+\cdot} + 2$), 307 (10, $M^{+\cdot} + 1$), 306 (55, $M^{+\cdot}$), 305 (10, $M^{+\cdot} - H$), 291 (5, $M^{+\cdot} - Me$), 277 (2, $M^{+\cdot} - CHO$), 262 ($M^{+\cdot} - CHO - Me$), 249 (1, $M^{+\cdot} - CHO - CO$), 234 ($M^{+\cdot} - CHO - Me - CO$), 221 (1), 220 (234 − N), 208 (2), 207 (1), 206 (1, 234 − 2N), 187 (3, $M^{+\cdot} - MeC_6H_4N_2$), 173 (19), 172 (100, $M^{+\cdot} - MeC_6H_4N_2$), 171 (2), 170 (1), 159 (2), 154 (3), 146 (7, $M^{+\cdot} - CHO - CN_2C_6H_4Me$), 131 (8), 119 (3, $MeC_6H_4N_2^+$), 118 (3), 117 (3), 107 (80, $Me_6H_4NH_2^+$), 106 (35, $MeC_6H_4NH^+$), 105 (6), 91 (35, $C_6H_4Me^+$), 90 (21), 79 (5), 78 (8), 77 (30, $C_6H_5^+$), 65 (15), 64 (6), 59 (4), 55 (3), and 51 (9).

*3-[2-(1,3-Diphenylimidazolidin-2-yl)-1-*p*-tolylhydrazono)glyoxal-1-yl]-2-quinoxalinone* (**13**). — A hot solution of compound **7** (0.6 g) in butanol (100 ml) was treated with *N,N'*-diphenyl-1,2-ethanediamine (0.42 g) in acetic acid (10 ml), and the mixture was refluxed for 1 h. The product that separated on cooling was recrystallized from ethanol in red needles (see Table II).

*3-{1,2-Bis[(*p*-iodophenyl)hydrazono]glyoxal-1-yl}-2-quinoxalinone* (**14**). — A hot solution of compound **10** (0.2 g) in butanol (100 ml) was treated with (*p*-iodophenyl)hydrazine (0.12 g), and the mixture was boiled under reflux for 15 min, whereupon the product separated out in yellow needles (see Table II).

3-[1-(Arylhydrazono)-2-(benzoylhydrazono)glyoxal-1-yl]-2-quinoxalinones (**15–19**). — A hot solution of compound **7–11** (0.1 g) in butanol (100 ml) was treated with the calculated amount of benzoylhydrazine, and the mixture was boiled under reflux for 15 min, whereupon the product separated out in yellow needles (see Table II).

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