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4-Phenyl-2,3-dioxobutyro-1,4-lactone (**1**) gave with phenylhydrazine and its *p*-Cl, *p*-Br, *p*-I and *p*-NO<sub>2</sub> derivatives, bishydrazones which were cyclized to 1-aryl-3-( $\alpha$ -hydroxybenzyl)-4,5-dione-4-arylhydrazones. With *o*-phenylene diamine, compound **1** gave either a Schiff base or a substituted quinoxaline, depending upon the ratio of the reactants.

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The hydrazine and *o*-phenylene diamine derivatives of dehydro-L-ascorbic acid have been converted into a multitude of heterocyclic compounds (1-5). In this paper we describe the preparation of the bisarylhydrazones of 4-phenyl-3,4-dioxobutyro-1,4-lactone and their conversion into pyrazolones as well as the reaction of 4-phenyl-2,3-dioxobutyro-1,4-lactone with *o*-phenylene diamine to give the Schiff base and a quinoxaline.

4-Phenyl-2,3-dioxobutyro-1,4-lactone (**1**) (6-10) the phenyl analog of dehydro-L-ascorbic acid, reacted readily with arylhydrazines to give bishydrazones (**2**). Like the bisaryl hydrazones of dehydro-L-acid, these compounds are red in color and their nmr spectra show two cheleated imino protons in the offset region of the spectrum. Thus, compound **2a** showed the imino protons at  $\delta$  10.99 and 11.98 ppm whereas dehydro-L-ascorbic acid bisphenylhydrazone shows the imino protons at  $\delta$  10.87 and 11.93 (11). The slight difference is probably due to deshielding by the phenyl ring in compound **2a**.

Upon treatment with sodium hydroxide bishydrazones **2a,c**, underwent lactone ring opening followed by nucleophilic attack on the carbonyl group by the nitrogen of the hydrazone residue attached to C-3. This resulted in the formation of the more stable pyrazolones (**3a,c**), which are analogs of the corresponding dehydro-L-ascorbic acid derivatives (**1**). The mass spectrum of compound **3a** was quite similar to that of the bishydrazones (**2a**) (see Figure 1). This is probably because bishydrazone **2a** underwent rearrangement upon electron impact and was converted into the more stable pyrazolone (**3a**). Both compounds showed practically the same fragmentation pattern, but the molecular peak of pyrazolones **3** was larger than that of the bishydrazone (**2**).

When phenyl 2,3-dioxobutaryl lactone (**1**) was treated with excess *o*-phenylene diamine the Schiff base (**4**) was obtained. However, when equimolar ratios of *o*-phenylene diamine and lactone **1** were reacted, the quinoxaline derivative (**5**) was obtained. The mass spectrum of compound **5** confirmed its structure. It showed a strong molecular

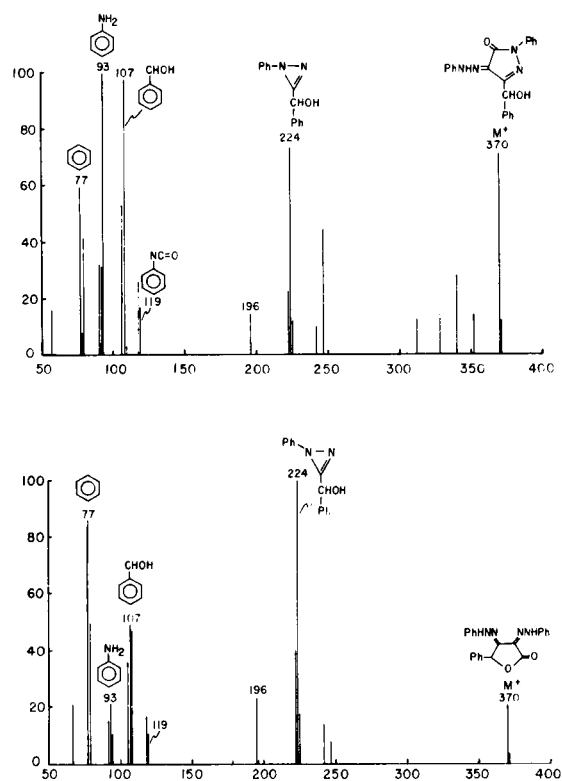


Figure 1 Mass Spectra of Compounds **4** and **3**.

peak followed by all the fragments expected from structure **5** (see Figure II). The analysis and the physical properties of the compounds prepared are shown in Table I.

#### EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. Microanalyses were carried out in the Department of Chemistry and Chemical Engineering, Michigan Technological University and the Chemistry Department, Cairo University. Nmr spectra were measured on a Varian HA 100 instrument and mass spectra on a Varian M 66 spectrometer.

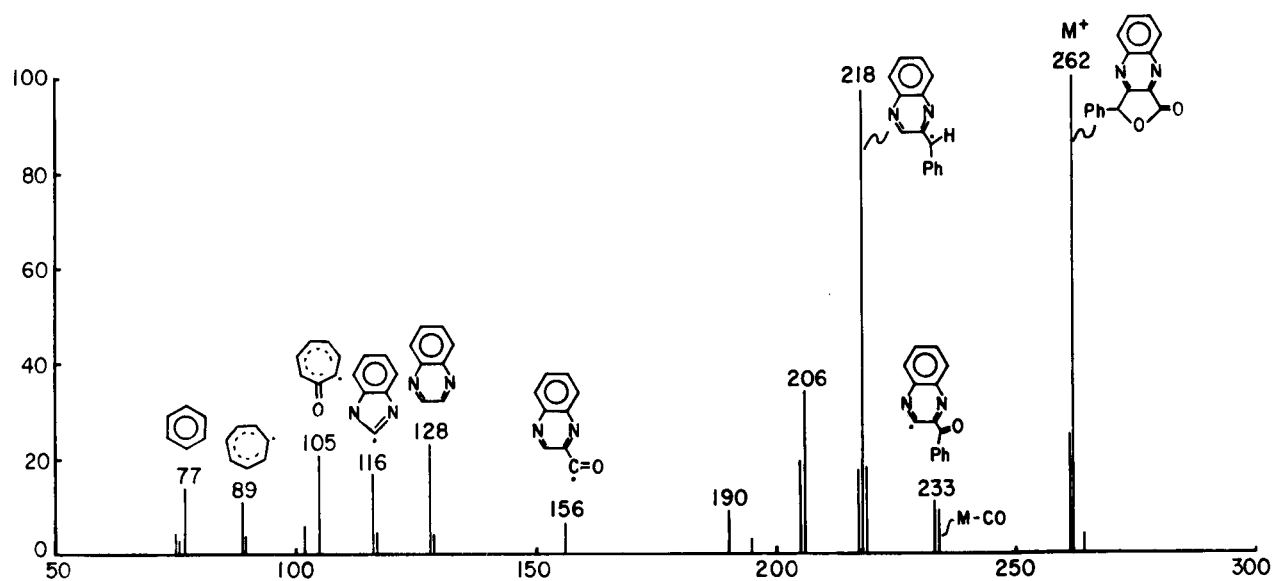
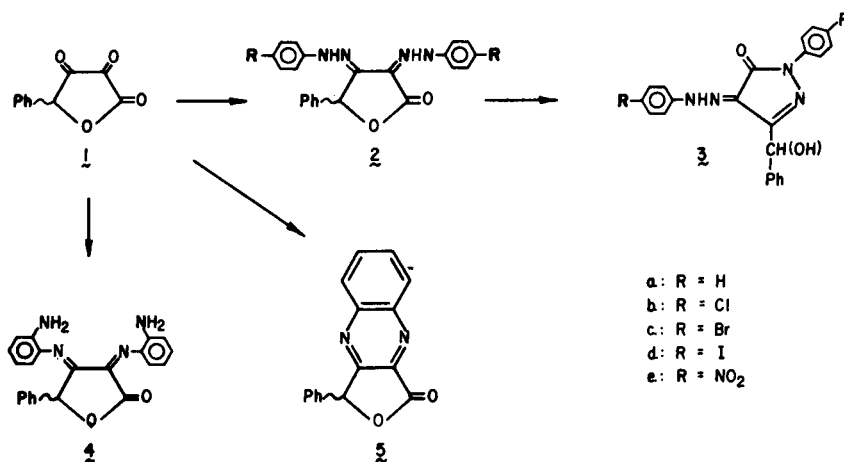


Figure II Mass Spectrum of Compound 5.

Table I

New Compounds Prepared

Compound No.	M.p. °C	Yield %	Formula	Calcd.			Found		
				C	H	N	C	H	N
2a	230	70	C <sub>22</sub> H <sub>18</sub> N <sub>4</sub> O <sub>2</sub>	71.3	4.9	15.1	71.6	5.1	14.9
2b	245	80	C <sub>22</sub> H <sub>16</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>2</sub>	60.2	3.7	12.8	60.1	4.0	12.9
2c	229	80	C <sub>22</sub> H <sub>16</sub> Br <sub>2</sub> N <sub>4</sub> O <sub>2</sub>	50.0	3.1	10.6	50.1	3.1	10.2
2d	247	80	C <sub>22</sub> H <sub>16</sub> I <sub>2</sub> N <sub>4</sub> O <sub>2</sub>	42.5	2.6	9.0	42.1	3.0	8.9
2e	252	75	C <sub>22</sub> H <sub>16</sub> N <sub>6</sub> O <sub>6</sub>	57.4	3.5	18.3	57.7	3.8	18.3
3a	160	75	C <sub>22</sub> H <sub>18</sub> N <sub>4</sub> O <sub>2</sub>	71.3	4.9	15.1	71.7	4.7	15.2
3c	213	70	C <sub>22</sub> H <sub>16</sub> Br <sub>2</sub> N <sub>4</sub> O <sub>2</sub>	50.0	3.1	10.6	50.2	3.1	10.5
4	194	75	C <sub>18</sub> H <sub>18</sub> N <sub>4</sub> O <sub>2</sub>	71.3	4.9	15.1	71.1	4.8	15.2
5	170	65	C <sub>22</sub> H <sub>18</sub> N <sub>4</sub> O <sub>2</sub>	73.3	3.8	10.7	73.1	3.8	11.0



## 4-Phenyl-2,3-dioxobutylolactone Bisarylhydrazones (II).

A solution of 4-phenyl-2,3-dioxobutylolactone (**1**) (6-10) (1 mmole) in water (15 ml.) and few drops of glacial acetic acid was heated with 2 mmoles of the desired arylhydrazines on a water bath for 2 hours. The red bisarylhydrazones that separated were filtered, washed with water, dried and crystallized from chloroform (see Table I).

1-Aryl-3-( $\alpha$ -hydroxybenzyl)-4,5-dione 4-Arylhydrazone (**3a,c**).

These compounds were obtained by heating bisarylhydrazones (**2a,c**) (1 g.) with 40 ml. of a 20% aqueous sodium hydroxide solution on a water bath for 15 minutes. Upon cooling and acidification with glacial acetic acid, the desired products separated out and were crystallized from dilute ethanol in orange needles (see Table I).

Schiff Base **4** and Quinoxaline (**5**).

A solution of 4-phenyl-2,3-dioxobutylolactone (**1**) (0.4 g.) in 10 ml. of ethanol containing two drops of glacial acetic acid was refluxed for one hour with *o*-phenylenediamine (0.44 g.) for compound **4**; or with 0.22 g. for compound **5**, dissolved in 10 ml. of ethanol. Upon concentration a yellow solid separated out which crystallized from ethanol in yellow needles.

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