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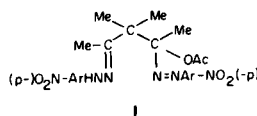
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Oxidation of the title bis-arylhydrazones **2** with silver oxide gives 1-aryl-5-aryloxy-3,4,4,5-tetramethyl-2-pyrazolines **4** in almost quantitative yield. The spectral data of the pyrazolines **4** as well as the reaction mechanism are discussed.

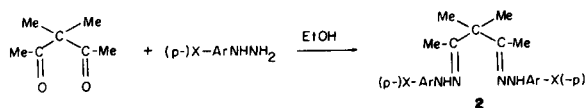
*J. Heterocyclic Chem.*, **20**, 431 (1983).

The bis-arylhydrazones of  $\alpha$ -dicarbonyl compounds are well known and their oxidation (1) to bis-azoethylenes and photo-oxidation (2) to 1,2,3-triazoles has been studied thoroughly. However, concerning the synthesis of bis-arylhydrazones of  $\beta$ -dicarbonyl compounds only those with 4-nitro- and 2,4-dinitro-phenylhydrazine have been reported (3-7).

Very recently Butler, *et al.*, have studied the oxidation (7) of bis-(4-nitrophenylhydrazones) of 1,3-diketones containing an  $\alpha$ -CH between the hydrazone chain either with lead tetraacetate or mercury (II) acetate which resulted in cyclization with fragmentation and formation of pyrazoles. Furthermore oxidation of 3,3-dimethylpentane-2,4-dione bis-(4-nitrophenylhydrazone) (**2d**) with lead tetraacetate gave 4-acetoxy-4-(4-nitrophenylazo)-3,3-dimethylpentan-2-one-4-nitrophenylhydrazone (**1**).

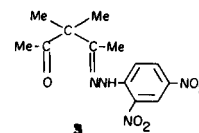


In the course of further work we have undertaken the preparation and oxidation with silver oxide of some bis-arylhydrazones of 3,3-dimethylpentane-2,4-dione **2**. The hydrazones **2** were prepared by reacting the diketone with the appropriate hydrazine in ethanol:



- a, X = H  
b, X = Me  
c, X = Cl  
d, X = NO<sub>2</sub>  
e, 2,4-dinitrophenyl-

However, the isolated product is not always the hydrazone **2** but the reaction product depends on the reaction temperature and the arylhydrazine. Analytically, in the case of the 4-nitro- and the 2,4-dinitrophenylhydrazine the corresponding bis-arylhydrazones **2d** and **2e** were isolated after refluxing the starting materials in ethanol for eight hours. In the case of the 2,4-dinitro-substituted compound the monohydrazone **3** was also isolated in 31% yield.



In contrast when the same reaction was repeated with the phenylhydrazine and the 4-methyl- and 4-chlorophenylhydrazine, the corresponding oxidation products, the 1-aryl-5-aryloxy-3,4,4,5-tetramethyl-2-pyrazolines **4a**, **4b** and **4c** only were formed. In addition, when the reaction was repeated at 20° with the 4-methyl- and 4-chlorophenylhydrazine both the bis-arylhydrazones **2b** and **2c** and their oxidation products the arylazopyrazolines **4b** and **4c** were isolated whereas with phenylhydrazine only the phenylazopyrazoline **4a** was formed.

The spectral and experimental data of the bis-arylhydrazones **2** are given in Table I.

It should be noticed at this point that the bis-arylhydrazone **2a** is reported (8) as a solid with mp 119-120°. However, detailed examination of the spectral data and especially the absence of an N-H absorption in the ir spectrum proves that the isolated compound with mp 107-109° corresponds to the cyclic arylazopyrazoline **4a** and not to the bis-arylhydrazone **2a**.

On the other hand it was reported previously (9) that the preparation of the 2,4-dinitrophenylhydrazone **2e** was an orange solid with mp 146°. Attempts to repeat the same reaction led to the isolation of two orange products, one with mp 141-143° and a second with mp 259-260°. The lower mp compound was attributed to the monohydrazone **3** and the higher mp compound to the bis-hydrazone **2e** on account to their spectral data and elemental analysis.

Oxidation of the bis-hydrazones **2** with silver oxide (1) in

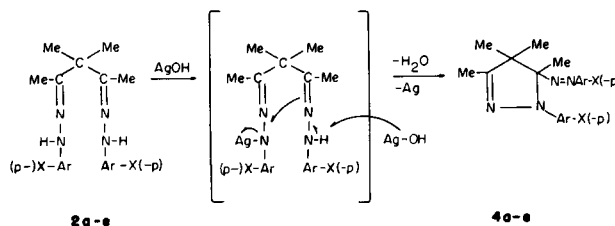


Table I  
Analytical Data for the Arylhydrazones **2**

Compound	Mp°C	Yield %	IR (Nujol) cm <sup>-1</sup>	NMR (Deuteriochloroform)			MS m/e (Relative Intensity, %)	Formula	Molecular Weight			Analysis %					
				δ C(Me) <sub>2</sub>	δ Me	p (δ-ArMe)			δ NH	δ aromatic protons	Calcd.	C	H	N	Found	C	H
<b>2b</b>	178-181	34	3350 3320	1.36 [6] s	1.65 [6] s	2.26 [6] s	—	6.94 [8] s	M <sup>+</sup> 336 (8) 215 (100) 106 (78)	C <sub>21</sub> H <sub>28</sub> N <sub>4</sub>	336.47	74.96	8.39	16.65	74.56	8.41	16.50
				1.42 [6] s	1.73 [6] s	—	6.18 [2] br s	ν <sub>A</sub> 7.16 ν <sub>B</sub> 7.31 <sup>(b), #</sup> J <sub>A,B</sub> 8 Hz	M <sup>+</sup> 380/378/ 376 (4) 237/235 (100) 129/127 (96)	C <sub>19</sub> H <sub>22</sub> Cl <sub>2</sub> N <sub>4</sub>	377.31	60.48	5.87	14.85	60.23	5.89	14.62
<b>2d</b>	221-223 (lit (7) mp 221-223)	62	3330	1.45 [3] s	1.82 [6] s	—	7.53 [2] br s	ν <sub>A</sub> 7.08 ν <sub>B</sub> 8.17 <sup>(b), #</sup> J <sub>A,B</sub> 8 Hz	M <sup>+</sup> 398 (-) 246 (28) 138 (36) 108 (100)	C <sub>19</sub> H <sub>22</sub> N <sub>4</sub> O <sub>6</sub>	398.41	57.28	5.57	21.10	57.30	5.58	20.97
				1.50 [3] s	2.03 [6] s	—	ν <sub>A</sub> 8.00 ν <sub>B</sub> 8.36 <sup>(a), #</sup> J <sub>A,B</sub> 9 Hz	(b)	C <sub>19</sub> H <sub>20</sub> N <sub>4</sub> O <sub>8</sub>	488.42	46.72	4.13	22.94	46.42	4.12	23.03	
<b>2e (a)</b>	259-260	54	3330	1.56 [6] s	2.03 [6] s	—	9.16 [2] d J 3 Hz										

(a) The nmr solvent was deuteriochloroform + 10% trifluoroacetic acid. (b) No adequate spectrum obtained up to 300°. (c) Further splitting was observed with J = 3 Hz.

Table II  
Analytical Data for the 1-Aryl-5-arylozo-3,4,4,5-tetramethyl-2-pyrazolines **4**

Compound	Mp°C	Yield %	NMR (Deuteriochloroform)		MS m/e (Relative Intensity, %)	Molecular Formula	Analysis %						
			$\delta$ 4,4-C(Me) <sub>2</sub>	$\delta$ 5-Me			$\delta$ 3-Me	Calcd.	Found				
<b>4a</b>	107-108	30 (a)	0.97 [3] s	1.55 [3] s	2.06 [3] s	C <sub>19</sub> H <sub>22</sub> N <sub>4</sub>	306.40	74.48	7.24	18.29	74.42	7.27	18.31
			1.22 [3] s	—	6.70-7.75 [10] m								
<b>4b</b>	83-84	97	0.87 [3] s	1.37 [3] s	1.95 [3] s	C <sub>21</sub> H <sub>26</sub> N <sub>4</sub>	334.45	75.41	7.84	16.75	75.26	7.87	16.66
			1.12 [3] s	2.18 [3] s	6.83 [4] s								
<b>4c</b>	105-106	95	0.88 [3] s	1.48 [3] s	2.00 [3] s	C <sub>19</sub> H <sub>20</sub> Cl <sub>2</sub> N <sub>4</sub>	375.30	60.80	5.37	14.93	60.40	5.55	14.68
			1.17 [3] s	—	7.02 [4] s								
<b>4d</b>	134-136	98	1.02 [3] s	1.80 [3] s	2.11 [3] s	C <sub>19</sub> H <sub>20</sub> N <sub>6</sub> O <sub>4</sub>	396.40	57.57	5.09	21.20	57.34	5.03	20.99
			1.28 [3] s	—	7.02 [4] s								
<b>4e</b>	169-170	96	1.05 [3] s	1.84 [3] s	1.99 [3] s	C <sub>19</sub> H <sub>18</sub> N <sub>6</sub> O <sub>5</sub>	486.40	46.90	3.73	23.04	46.60	3.69	22.99
			1.29 [3] s	—	7.02 [4] s								

(a) The yield is referred to the preparation from the diketone and phenylhydrazine. (b) The doublets at 8.07 and 8.44 show additional splitting with J = 3 Hz. (c) J = 3 Hz. (d) No adequate spectrum obtained up to 300°.

dry ether or tetrahydrofuran at 25° leads to the formation of 1-aryl-5-arylo-3,4,4,5-tetramethyl-2-pyrazolines **4** in almost quantitative yield.

In the first step of the reaction sequence a bond between one of the N-H groups and silver is formed. Cleavage of the N-Ag bond results in the formation of the arylazopyrazolines **4**.

The spectral and experimental data for the arylazopyrazolines **4** are given in Table II and are in agreement with the proposed structure, namely four singlets are observed in the <sup>1</sup>H nmr spectrum for the four methyl groups and an absorption with  $\lambda$  max at approximately 430 nm in the uv spectrum thus indicating the presence of an azo group. In the mass spectra molecular ion is not observed but a high intensity peak corresponding to the ion  $[M-(p)X-ArN_2]^+$  or  $[M-(p)X-ArN_2H]^+$ .

The isolation of the arylazopyrazolines **4** proves that the two hydrazone groups do not behave independently as in the case of the lead tetraacetate oxidation (7). These compounds **4** are completely analogous to the arylazopyrazolines isolated (10) by the oxidation of bis-arylohydrazones of 3,3-dimethylpentane-2,4-dione with lead tetraacetate. However, from the thermal decomposition (10,11) of the arylazopyrazolines **4** only biphenyl and unidentified compounds were isolated.

## EXPERIMENTAL

All melting points are uncorrected and they were obtained with a Kofler hot stage apparatus. Ir spectra were obtained with a Perkin-Elmer Model 257, whereas nmr spectra reported in  $\delta$  units with a Varian Associates CFT-20 spectrometer with TMS as internal reference. The mass spectra were obtained with a Hitachi-Perkin-Elmer Model RMU-6L spectrometer with ionization energy 70eV. Analysis were performed with a Perkin Elmer Model 240 CHN Analyser.

Preparation of 3,3-Dimethylpentane-2,4-dione Bis-(4-methylphenylhydrazone) (**2b**).

A solution of 0.01 mole 3,3-dimethylpentane-2,4-dione and 0.022 mole 4-methylphenylhydrazine in 20 ml ethanol was stirred at 20° for 70 hours. The white solid which was formed was filtered and recrystallized from ethanol to give the 3,3-dimethylpentane-2,4-dione bis-(4-methylphenylhydrazone) (**2b**) in 34% yield. When the filtrate was reduced to 5 ml the yellow 1-(4-methylphenyl)-5-(4-methylphenylazo)-3,4,4,5-tetramethyl-2-pyrazoline (**4b**) was precipitated and recrystallized from ethanol; yield 25%. However, when the reaction was repeated with reflux in ethanol only the cyclic arylazopyrazoline **4b** was isolated in 48% yield.

Preparation of 3,3-Dimethylpentane-2,4-dione Bis-(4-chlorophenylhydrazone) (**2c**).

The procedure described above was followed and the 3,3-dimethylpentane-2,4-dione bis-(4-chlorophenylhydrazone) (**2c**) and the 1-(4-chlorophenyl)-5-(4-chlorophenylazo)-3,4,4,5-tetramethyl-2-pyrazoline (**4c**) were isolated in 10% and 72% yield, respectively. When the reaction was repeated under reflux again only the arylazopyrazoline **4c** was isolated in 65% yield.

Preparation of 3,3-Dimethylpentane-2,4-dione Bis-(4-nitrophenylhydrazone) (**2d**).

A solution of 0.01 mole of 3,3-dimethylpentane-2,4-dione and 0.022 mole 4-nitrophenylhydrazine in 30 ml ethanol was refluxed for 8 hours. Upon cooling the 3,3-dimethylpentane-2,4-dione bis-(4-nitrophenylhydrazone) (**2d**) was crystallized as a yellow solid in 62% yield. Recrystallization from ethanol.

Preparation of 3,3-Dimethylpentane-2,4-dione Bis-(2,4-dinitrophenylhydrazone) (**2e**) and 3,3-Dimethylpentane-2,4-dione Mono-(2,4-dinitrophenylhydrazone) (**3**).

The procedure described above was followed and the 3,3-dimethylpentane 2,4-dione bis-(2,4-dinitrophenylhydrazone) (**2e**) was precipitated as an orange solid in 54% yield and was purified by refluxing in ethanol. The combined ethanol filtrates were evaporated to dryness and the solid which was left behind was refluxed with 50 ml ether. The ether filtrate was evaporated and the remainder was recrystallized from petroleum ether to give the 3,3-dimethylpentane-2,4-dione mono-(2,4-dinitrophenylhydrazone) (**3**) in 31% yield, orange solid, mp 141-143°; ir (nujol): 3320, 1720, 1630  $\text{cm}^{-1}$ ; nmr (deuteriochloroform):  $\delta$  1.44 (s, 6H, C(Me)<sub>2</sub>), 2.00 (s, 3H, Me), 2.14 (s, 3H, COMe), 7.90 and 8.29 (two d, J = 9 Hz, 2H, aromatic, the doublet at 8.29 also shows additional splitting with J = 3 Hz), 9.09 (d, J = 3 Hz, 1H, aromatic) and 11.01 (br s, 1H, NH).

Anal. Calcd. for C<sub>13</sub>H<sub>16</sub>N<sub>4</sub>O<sub>5</sub>: C, 50.64; H, 5.23; N, 18.18. Found: C, 50.72; H, 5.34; N, 18.19.

Preparation of 1-Phenyl-5-phenylazo-3,4,4,5-tetramethyl-2-pyrazoline (**4a**).

A solution of 0.01 mole of 3,3-dimethylpentane-2,4-dione and 0.022 mole phenylhydrazine in 20 ml ethanol was stirred at 25° for 36 hours. The solution was then reduced to 5 ml to give the yellow 1-phenyl-5-phenylazo-3,4,4,5-tetramethyl-2-pyrazoline (**4a**) in 30% yield. Recrystallization was from ethanol.

Oxidation of the Bis-arylohydrazones **2** With Silver Oxide. Formation of 1-Aryl-5-arylo-3,4,4,5-tetramethyl-2-pyrazolines (**4**).

A general procedure (1) is described. To a solution of 0.001 mole of the bis-hydrazone **2** in 15 ml dry ether or tetrahydrofuran, 0.004 mole silver oxide was added. The reaction mixture was refluxed for 15 hours and then filtered to remove the inorganic material. The filtrate was evaporated to 3 ml and the arylazopyrazoline **4** was crystallized (Table II). Recrystallization was from ethanol.

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