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Oxidation of the title bis-aryldiazones **2** with lead tetraacetate gives 1-aryl-5-aryldiazo-3,4,4,5-tetra-methyl-2-pyrazolines **6** in good yields. The aryldiazopyrazolines **6** decompose by refluxing in chloroform or ethanol solution to 1-aryl-5-hydroxy-3,4,4,5-tetramethyl-2-pyrazolines **3**, 1-aryl-5-methylene-3,4,4-trimethyl-2-pyrazoles **10** and 1-aryl-3,4,4,5-tetramethyl-2-pyrazolines **11**. The spectral data of the prepared compounds, as well as the reaction mechanisms are discussed.

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Although the bis-aryldiazones of α -dicarbonyl compounds are well known and their oxidation (2) to triazolylisoimides has been studied thoroughly the bis-aryldiazones of β -dicarbonyl compounds are almost completely unknown. It is also of interest to note that the mono-aryldiazones of β -di-carbonyl compounds are

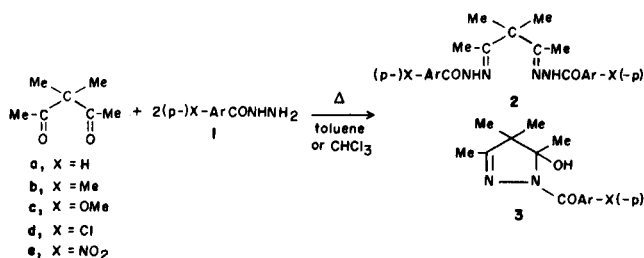
not easily isolated because they tend to form (3) pyrazole derivatives.

For the reasons mentioned above we have undertaken the preparation of some bis-aryldiazones **2** of 3,3-dimethylpentane-2,4-dione according to the following scheme:

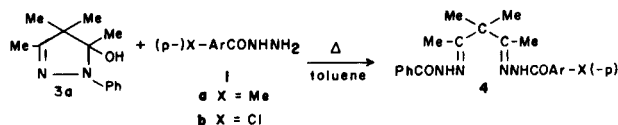
Table I
 Analytical Data for the Bis-aryldiazones **2** and **4**

Compound	Mp °C	Yield %	IR (Nujol) cm ⁻¹		MS m/e (Relative intensity %)	Formula	Molecular Weight	Analysis %					
			ν NH	ν CO				Calcd.			Found		
							C	H	N	C	H	N	
2a	136-139	22	3280 3340	1690	M ⁺ 364 (<0.5) 228 (100) 213 (60) 199 (51) 136 (100) 105 (100)	C ₂₁ H ₂₄ N ₄ O ₂	364.4	69.21	6.64	15.38	69.18	6.62	15.40
2b	161-164	19	3300 3340	1680	M ⁺ 392 (<0.5) 242 (31) 119 (100)	C ₂₃ H ₂₈ N ₄ O ₂	392.5	70.38	7.19	14.28	70.28	7.20	14.18
2c	141-144	34	3300 3370	1685	M ⁺ 424 (-) 258 (12) 243 (18) 135 (100)	C ₂₃ H ₂₈ N ₄ O ₄	424.5	65.07	6.65	13.20	65.09	6.69	13.19
2d	145-148	17	3280	1655	M ⁺ 436/434/432 (-) 264/262 (34) 249/247 (4) 235/233 (3) 141/139 (100)	C ₂₁ H ₂₂ Cl ₂ N ₄ O ₂	433.3	58.20	5.12	12.93	58.31	5.09	12.94
2e	202-204	38	3310 3370	1655 1665	(a)	C ₂₁ H ₂₂ N ₆ O ₆	454.4	55.50	4.88	18.50	55.27	4.83	18.24
4a	132-135	39	3300 3360	1680	M ⁺ 378 (-) 243 (69) 229 (64) 119 (100) 105 (91)	C ₂₂ H ₂₆ N ₄ O ₂	378.5	69.81	6.92	14.81	70.01	6.88	14.61
4b	126-129	46	3290 3350	1650 1680	M ⁺ 400/398 (2) 265/263 (20) 229 (22) 141/139 (100) 105 (100)	C ₂₁ H ₂₃ ClN ₄ O ₂	398.9	63.23	5.81	14.05	63.51	5.85	13.97

(a) No adequate spectrum obtained up to 300°.



The 1-aryl-5-hydroxy-3,4,4,5-tetramethyl-2-pyrazolines (**3**) which were isolated during the preparation of the bis-acylhydrazones (**2**) were used for the preparation of the unsymmetrically substituted hydrazones **4**.



The spectral and experimental data for the bis-acylhydrazones **2** and **4** are given in Table I. In the ¹H nmr spectra they show two singlets between δ 1.20-1.27 for the protons of the two methyl groups attached to the central carbon atom. Two singlets at approximately δ 1.50 and 1.93 are also observed for the protons of the other two methyl groups. The two protons of the two NH groups (deuterium oxide exchangeable) are observed approximately at δ 4.75 and 9.40 leading to the conclusion (4,5) that the signal observed at low field corresponds to a hydrogen which most probably forms a hydrogen bond with a second nitrogen as shown below.

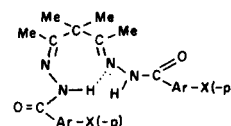


Table II

Analytical Data for the 1-Aroyl-5-hydroxy-3,4,4,5-tetramethyl-2-pyrazolines **3**

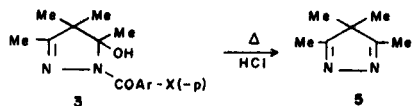
Compound	Mp °C	Yield %	IR (Nujol) cm ⁻¹		MS m/e (Relative intensity %)	Formula	Molecular Weight	Analysis %					
			ν NH	ν CO				Calcd.			Found		
								C	H	N	C	H	N
3a	158-161	51	3430	1650	M ⁺ 246 (47) 231 (11) 204 (20) 203 (7) 161 (18) 141 (3) 105 (100)	C ₁₄ H ₁₈ N ₂ O ₂	246.3	68.27	7.37	11.37	68.32	7.37	11.40
3b	159-161	61	3420	1660	M ⁺ 260 (48) 245 (9) 218 (10) 217 (7) 175 (20) 141 (4) 119 (100)	C ₁₄ H ₂₀ N ₂ O ₂	260.3	69.20	7.74	10.76	69.29	7.75	10.80
3c	103-105	52	3460	1650	M ⁺ 276 (42) 261 (5) 234 (3) 233 (6) 191 (69) 141 (2) 135 (100)	C ₁₅ H ₂₀ N ₂ O ₃	276.3	65.19	7.30	10.14	65.13	7.31	10.16
3d	142-144	56	3430	1660	M ⁺ 282/280 (37) 267/265 (11) 240/238 (24) 239/237 (10) 197/195 (35) 141/139 (100)	C ₁₄ H ₁₇ ClN ₂ O ₂	280.8	59.89	6.10	9.98	60.02	6.09	10.01
3e	138-139	34	3420	1660	M ⁺ 291 (47) 276 (16) 249 (56) 248 (12) 206 (67) 150 (100) 141 (4)	C ₁₄ H ₁₇ N ₄ O ₄	291.3	57.72	5.88	14.43	57.69	5.86	14.50

In the mass spectra the molecular ion whenever it is observed is a very low intensity peak. However a very high intensity peak corresponding to the ions $[M-(p-)X-ArCONHNH_2]^+$ or $[M-(p-)X-ArCONHNH]^+$ is always observed.

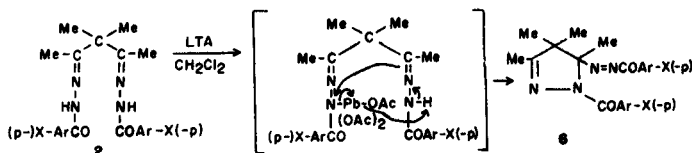
The spectral and experimental data for the 1-aryl-5-hydroxy-3,4,4,5-tetramethyl-2-pyrazolines **3** are given in Table II. In the 1H nmr spectra the protons of the two methyl groups in the 4-position of the heterocyclic ring show two singlets, one at approximately δ 1.12 and the second at approximately δ 1.18. The protons of the other two methyl groups in the 3- and 5-position of the five-membered ring also show two singlets at approximately δ 1.93 and 1.72, respectively, whereas for the hydroxyl proton (deuterium oxide exchangeable) a broad singlet at approximately δ 4.92 is observed.

In the mass spectra they show a high intensity peak for the molecular ion. Other prominent peaks are those corresponding to the ions $[M-(CH_3)_2CCOCH_3]^+$ $[M-CH_2=C=O]^+$ and $(p-)X-Ar^+CO$ which is the base peak of the spectra.

The hydroxypyrazolines **3** give upon treatment (6) with hydrochloric acid the 3,4,4,5-*H*-pyrazole **5**.



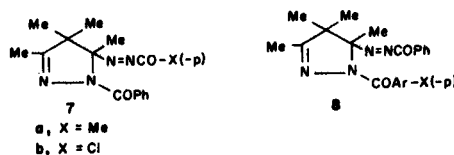
Oxidation of the bis-aryldrazones **2** with lead tetraacetate (LTA) at room temperature leads to the formation of 1-aryl-5-aryloxy-3,4,4,5-tetramethyl-2-pyrazolines **6** in 65-90% yield.



In the first step of the reaction sequence a bond between the one of the N-H groups and lead is formed (7). Cleavage of the N-Pb bond and loss of acetic acid results to the formation of the aroylazopyrazolines **6**.

The spectral and experimental data for the aroylazopyrazolines **6** are given in Tables III-IV and are in agreement with the proposed structure, namely in the ir spectrum two carbonyl absorptions at approximately 1650 and 1710 cm^{-1} are observed and also two signals at approximately 162 and 181 ppm in the ^{13}C nmr spectrum. In addition four singlets are observed both in the 1H and ^{13}C nmr for the four methyl groups. In the mass spectra the molecular ion is not observed but a high intensity peak corresponding to the ion $[M-(p-)X-ArCON_2]^+$.

In the case of oxidation of the unsymmetrically substituted bis-aryldrazones **4** two isomeric aroylazopyrazolines **7** and **8** can be formed.



From the oxidation of the bis-aryldrazones **4a** the two isomeric aroylazopyrazolines **7a** and **8a** were isolated and identified from their thermal decomposition products (see further discussion and the experimental), whereas in the case of the bis-aryldrazones **4b** the separation of the isomeric aroylazopyrazolines **7b** and **8b** was not successful. The spectral and experimental data for the compounds **7** and **8** are given in Tables III and V.

The aroylazopyrazolines **6** are unstable compounds and decompose (8) even at room temperature. The decomposition is more efficient by refluxing in chloroform solution and even more by refluxing in ethanol solution. The decomposition products are *p*-substituted ethyl benzoates **9**,

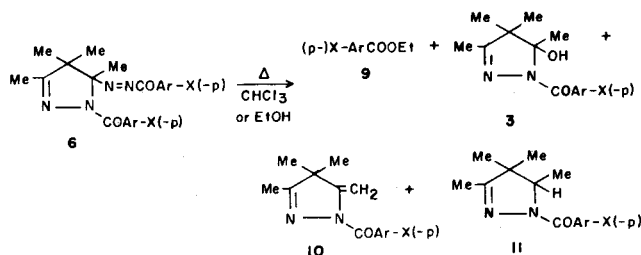
Table III

 1H NMR Chemical Shifts of the Aroylazopyrazolines **6**, **7** and **8** (a,b)

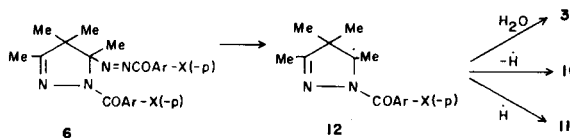
Compound	4,4-Me	3,5-Me	Aromatic protons	(<i>p</i> -)Me	OMe						
(6a)	1.03 [3] s	1.22 [3] s	1.82 [3] s	2.02 [3] s	7.00-8.00 [10] m	—	—	—	—		
(6b)	1.04 [3] s	1.18 [3] s	1.80 [3] s	2.08 [3] s	7.20-7.47 [4] two d (c)	7.63-8.08 [4] two d (c)	J 8 Hz	2.30 [3] s	2.35 [3] s	—	—
(6c)	1.10 [3] s	1.27 [3] s	1.88 [3] s	2.12 [3] s	6.79-7.00 [4] two d (c)	7.73-8.00 [4] two d (c)	J 9 Hz	—	—	3.80 [3] s	3.85 [3] s
(6d)	1.09 [3] s	1.28 [3] s	1.90 [3] s	2.12 [3] s	7.27-8.02 [8] seven s	—	—	—	—	—	—
(6e)	1.10 [3] s	1.32 [3] s	1.88 [3] s	2.14 [3] s	7.89, 8.18 [4] two d	8.23, 8.35 [4] two d	J 8 Hz	—	—	—	—
(7a)	1.13 [3] s	1.30 [3] s	1.90 [3] s	2.17 [3] s	7.10-8.15 [5] m	7.21 and 7.49 [4] two d	J 9 Hz	2.43 [3] s	—	—	—
(8a)	1.12 [3] s	1.28 [3] s	1.90 [3] s	2.17 [3] s	7.31-8.02 [5] m	7.22 and 7.73 [4] two d	J 8 Hz	2.38 [3] s	—	—	—

(a) δ in ppm. (b) Solvent deuteriochloroform. (c) Two AB systems are observed but not analysed.

1-aryl-5-hydroxy-3,4,4,5-tetramethyl-2-pyrazolines **3**, 1-aryl-5-methylene-3,4,4-trimethyl-2-pyrazoles **10** and 1-aryl-3,4,4,5-tetramethyl-2-pyrazolines **11** as shown in the following scheme.



For the formation of the decomposition products a free radical mechanism could be suggested:



In the first step of the reaction sequence elimination of the aroylazo group leads to the formation of the pyrazoline radical **12** from which the products **3**, **10** and **11** can be obtained.

The hydroxypyrazolines **3** were also isolated during the preparation of the bis-arylhazones **2** and have been already discussed.

The 1-aryl-5-methylene-3,4,4-trimethyl-2-pyrazoles **10** give in the ^1H nmr spectrum one singlet at approximately δ 1.25 for the protons of the two methyl groups in the 4-position of the heterocyclic ring, one singlet at approximately δ 1.94 for the protons of the third methyl group and two doublets centered at approximately δ 4.65 and 6.10 ($J \sim 1$ Hz) for the methylene protons. In the mass spectra they show the typical fragmentation pattern of the pyrazoles. Thus, the high intensity peak of the molecular ion is followed by the less intensive peak $[\text{M} - \text{CH}_3\text{CN}]^+$. The analytical data for the methylene pyrazoles **10** are given in Table VI.

The 1-aryl-3,4,4,5-tetramethyl-2-pyrazolines **11** show in the ^1H nmr spectrum two singlets for the protons of the

methyl groups in the 4-position of the heterocyclic ring at approximately δ 1.10 one singlet for the protons of the methyl group in the 3-position at approximately δ 1.87 one doublet for the protons of the methyl group in the 5-position at approximately δ 1.28 and a quartet for the 5-position proton at approximately δ 4.25. In the mass spectra they also show a typical pyrazolinic fragmentation pattern, namely a high intensity peak for the molecular ion followed by the less intensive peak $[\text{M} - \text{CH}_3\text{CN}]^+$. Their analytical data are given in Table VII.

EXPERIMENTAL

All melting points are uncorrected and they are obtained with a Kofler hot stage apparatus. The ir spectra were obtained with a Perkin-Elmer Model 297, whereas nmr spectra reported in δ units with a Varian Associates CFT-20 spectrometer with TMS as internal reference. The mass spectra were obtained with Hitachi-Perkin-Elmer Model RMU-6L spectrometer with ionization energy 70eV. Analyses were performed with a Perkin-Elmer Model 240 CHN Analyser.

Preparation of bis-Aroylhazones of 3,3-Dimethylpentane-2,4-dione (**2**) and 1-Aroyl-5-hydroxy-3,4,4,5-tetramethyl-2-pyrazolines **3**.

A general procedure (**2**) is described. A solution of 0.01 mole of 3,3-dimethylpentane-2,4-dione and 0.022 moles of the corresponding aroylhydrazine **1** was refluxed in chloroform or toluene (50 ml) for 20 hours. The residue which was left behind after evaporation of the solvent was subjected to column chromatography on silica gel (petroleum ether-ethyl acetate 1:1) to give as the first component the 1-aryl-5-hydroxy-3,4,4,5-tetramethyl-2-pyrazoline **3** and as the second component the bis-arylhazone **2**. The ^1H nmr spectral data of the bis-arylhazones **2** and the hydroxypyrazolines **3** in deuteriochloroform solution are given below, while the rest of the experimental data are given in Tables I and II, respectively.

Compound 2a.

This compound had nmr: δ 1.22 and 1.27 (two s, 6H, $\text{C}(\text{Me})_2$), 1.52 and 1.93 (two s, 6H, Me), 4.75 and 9.51 (two br s, 2H, NH), 7.26-8.06 (m, 10H, aromatic).

Compound 2b.

This compound had nmr: δ 1.22 and 1.27 (two s, 6H, $\text{C}(\text{Me})_2$), 1.50 and 1.93 (two s, 6H, Me), 2.38 (s, 6H, ArMe), 4.75 and 9.43 (two br s, 2H, NH) and 7.10-7.93 (four d, $J = 8$ Hz, 8H, aromatic).

Compound 2c.

This compound had nmr: δ 1.21 and 1.27 (two s, 6H, $\text{C}(\text{Me})_2$), 1.50 and 1.94 (two s, 6H, Me), 3.80 (s, 6H, OMe), 4.76 and 9.41 (two br s, 2H, NH), and 6.75-7.95 (four d, $J = 9$ Hz, 8H, aromatic).

Compound 2d.

This compound had nmr: δ 1.22 and 1.27 (two s, 6H, $\text{C}(\text{Me})_2$), 1.48 and 1.94 (two s, 6H, Me), 4.73 and 9.55 (two br s, 2H, NH), and 7.20-7.90 (four

Table IV

^{13}C NMR Chemical Shifts of the Aroylazopyrazolines **6** (a,b,c)

Compound	4,4-CH ₃	5-CH ₃	3-CH ₃	5-C	3-C	N-CO	N=NCO	
6a	16.66	16.75	11.98	22.52	53.17	96.16	160.82	181.54
6b	15.85	16.00	11.21	21.50	54.18	95.05	159.50	181.94
6c	15.96	16.12	11.26	21.62	54.27	95.17	164.00	181.31

(a) Values in ppm from internal tetramethylsilane. (b) Solvent deuteriochloroform. (c) The 4-C is missing probably superimposed with CH₃.

d, $J = 9$ Hz, 8H, aromatic).

Compound **2e**.

This compound had nmr: (deuteriochloroform + 10% trifluoroacetic acid): δ 1.52 (s, 6H, C(Me)₂), 2.52 (s, 6H, Me) and 7.03-7.65 (m, 8H, aromatic).

Compound **3a**.

This compound had nmr: δ 1.12 and 1.19 (two s, 6H, C(Me)₂), 1.74 (s, 3H, 5-Me), 1.93 (s, 3H, 3-Me), 4.92 (br, s, 1H, OH) and 7.27-7.97 (m, 5H, aromatic).

Compound **3b**.

Table V

Analytical Data for the Aroylazopyrazolines **6**, **7** and **8**

Compound	Mp °C	Yield %	IR (Nujol) cm ⁻¹		MS m/e (Relative intensity %)	Formula	Molecular Weight	Analysis %					
			ν NH	ν CO				Calcd.		Found			
								C	H	N	C	H	N
6a	108-109	92	1655	1705	M ⁺ 362 (-) 229 (30) 214 (50) 173 (18) 105 (100)	C ₂₁ H ₂₂ N ₄ O ₂	362.4	69.59	6.12	15.46	69.61	6.15	15.45
6b	133-136	80	1650	1715	M ⁺ 390 (-) 243 (39) 228 (38) 187 (10) 119 (100)	C ₂₃ H ₂₆ N ₄ O ₂	390.5	70.47	6.71	14.35	70.73	6.74	14.43
6c	139-141	85	1655	1700	M ⁺ 422 (-) 259 (30) 244 (18) 203 (9) 135 (100)	C ₂₃ H ₂₆ N ₄ O ₄	422.5	65.38	6.20	13.26	65.50	6.20	13.26
6d	140-142	66	1645	1720	M ⁺ 434/432/430 (-) 265/263 (19) 250/248 (9) 209/207 (7) 141/139 (100)	C ₂₁ H ₂₀ Cl ₂ N ₄ O ₂	431.3	58.48	4.67	12.99	58.52	4.58	12.99
6e	177-178	86	1660	1720	M ⁺ 452 (-) 274 (48) 259 (11) 218 (7) 150 (100)	C ₂₁ H ₂₀ N ₆ O ₆	452.4	55.75	4.46	18.58	55.81	4.31	18.37
7a (a)	95-99	38	1660	1715	M ⁺ 376 (-) 229 (31) 214 (28) 173 (15) 119 (100)	C ₂₂ H ₂₄ N ₄ O ₂	376.4	70.18	6.43	14.88	70.40	6.60	15.02
8a (a)	102-107	31	1655	1720	M ⁺ 376 (-) 243 (29) 228 (35) 187 (21) 105 (100)	C ₂₂ H ₂₄ N ₄ O ₂	376.4	70.18	6.43	14.88	69.99	6.40	14.79
7b + 8b	86-91	25	1660	1715	M ⁺ 398/396 (-) 265/263 (18) 229 (21) 250/248 (12) 214 (14) 209/207 (9) 173 (3) 141/139 (70) 105 (100)	C ₂₁ H ₂₁ ClN ₄ O ₂	396.9	63.55	5.33	14.12	63.48	5.46	14.01

(a) The overall reaction yield is 69%.

Table VI
Analytical Data for the 1-Aroyl-5-methylene-3,4,4-trimethyl-2-pyrazoles **10**

Compound	Mp °C	Yield %	IR ν CO cm ⁻¹ (Nujol)	NMR (Deuteriochloroform)			MS m/e	Formula	Molecular Weight	Analysis %							
				δ CH ₂	δ 4,4-Me	δ 3-Me				δ aromatic protons	δ (p-)Me	Calcd.	Found				
10a	111-113	16	1660	ν_A 4.64	1.23 [6] s	1.93 [3] s	M ⁺ 228 (39) 213 (3) 209 (2) 187 (3) 105 (100)	C ₁₄ H ₁₆ N ₂ O	228.3	73.65	7.06	12.27	73.60	6.92	12.03		
				ν_X 6.09 ^{(2),K} system J _{AX} 0.8 Hz		7.05-7.50 [3] m 7.55-7.90 [2] m											
10b	127-128	7	1650	ν_A 4.61	1.25 [6] s	1.95 [3] s	M ⁺ 242 (34) 227 (2) 213 (2) 201 (4) 119 (100)	C ₁₅ H ₁₈ N ₂ O	242.3	74.35	7.49	11.56	73.99	7.55	11.33		
				ν_X 6.07 ^{(2),K} system J _{AX} 0.8 Hz		ν_A 7.13 ν_B 7.63 ^{(4),#} system J _{AB} 10 Hz											2.43 [3] s
10d	111-114	48	1660	ν_A 4.65	1.25 [6] s	1.94 [3] s	M ⁺ 264/262 (55) 249/247 (7) 235/233 (6) 223/221 (5) 141/139 (100)	C ₁₄ H ₁₅ ClN ₂ O	262.7	63.99	5.75	10.66	63.69	5.81	10.78		
				ν_X 6.09 ^{(2),K} system J _{AX} 0.8 Hz		ν_A 7.31 ν_B 7.78 ^{(4),#} system J _{AB} 9 Hz											—
10e	120-122	14	1660	ν_A 4.73	1.31 [6] s	1.94 [3] s	M ⁺ 273 (23) 258 (8) 244 (7) 150 (100)	C ₁₄ H ₁₅ N ₃ O ₃	273.3	61.53	5.53	15.38	61.33	5.63	14.99		
				ν_X 6.14 ^{(2),K} system J _{AX} 1.0 Hz		ν_A 7.76 ν_B 8.20 ^{(4),#} system J _{AB} 9 Hz											—

Table VII

Analytical Data for the 1-Aroyl-3,4,4,5-tetramethyl-2-pyrazolines II.

Compound	Mp °C	Yield %	IR (Nujol) cm ⁻¹	NMR (Deuteriochloroform)				MS m/e (Relative Intensity %)	Formula	Molecular Weight	Analysis %					
				δ 4,4-Me	δ 5-Me	δ 3-Me	δ 5-H				δ (p-)Me	δ OMe	Calcd.	Found		
IIa	71-73	51	1635 ν CO	δ 4,4-Me 1.08 [3] s 1.10 [3] s	δ 5-Me 1.29 [3] d(a) 1.87 [3] s	δ 3-Me 1.87 [3] s	δ 5-H 4.24 [1] q(a) 7.25-7.50 [3] m 7.60-7.87 [2] m	M ⁺ 230 (41) 215 (6) 189 (7) 188 (3) 174 (7) 105 (100)	C ₁₁ H ₁₄ N ₂ O	230.3	73.01	7.88	12.17	73.29	7.96	12.22
IIb	oil	41	1645	1.11 [3] s 1.13 [3] s	1.28 [3] d(a) 1.87 [3] s	1.87 [3] s	4.25 [1] q(a) 7.73 ^{(a), (b)} 7.73 ^{(a), (b)} J _{A,B} 9 Hz	M ⁺ 244 (37) 229 (4) 203 (7) 202 (2) 188 (6) 119 (100)	C ₁₁ H ₁₀ N ₂ O	244.3	73.73	8.25	11.47	73.65	8.05	11.19
IIc	oil	16	1645	1.08 [3] s 1.10 [3] s	1.27 [3] d(a) 1.86 [3] s	1.86 [3] s	4.21 [1] q(a) 7.82 ^{(a), (b)} 7.74 ^{(a), (b)} J _{A,B} 9 Hz	M ⁺ 260 (15) 245 (2) 219 (2) 218 (8) 204 (8) 135 (100)	C ₁₁ H ₁₀ N ₂ O ₂	260.3	69.20	7.74	10.76	68.87	7.82	10.37
IIId	109-111	23	1645	1.10 [3] s 1.12 [3] s	1.25 [3] d(a) 1.87 [3] s	1.87 [3] s	4.21 [1] q(a) 7.74 ^{(a), (b)} 7.74 ^{(a), (b)} J _{A,B} 9 Hz	M ⁺ 266/264 (7) 225/223 (28) 210/208 (27) 141/139 (100)	C ₁₁ H ₁₁ ClN ₂ O	264.8	63.51	6.48	10.51	63.34	6.31	10.50

(a) J = 7 Hz.

This compound had nmr: δ 1.12 and 1.18 (two s, 6H, C(Me)₂), 1.70 (s, 3H, 5-Me), 1.93 (s, 3H, 3-Me), 2.39 (s, 3H, ArMe), 4.93 (br s, 1H, OH) and 7.16 and 7.74 (AB-system, J = 8 Hz, 4H, aromatic).

Compound 3c.

This compound had nmr: δ 1.08 and 1.14 (two s, 6H, C(Me)₂), 1.67 (s, 3H, 5-Me), 1.89 (s, 3H, 3-Me), 3.77 (s, 3H, OMe), 4.93 (br s, 1H, OH), and 6.83 and 7.81 (AB-system, J = 9 Hz, 4H, aromatic).

Compound 3d.

This compound had nmr: δ 1.14 and 1.19 (two s, 6H, C(Me)₂), 1.74 (s, 3H, 5-Me), 1.97 (s, 3H, 3-Me), 4.93 (br s, 1H, OH) and 7.42 and 7.86 (AB system, J = 9 Hz, 4H, aromatic).

Compound 3e.

This compound had nmr: δ 1.11 and 1.16 (two s, 6H, C(Me)₂), 1.72 (s, 3H, 5-Me), 1.88 (s, 3H, 3-Me), 4.52 (br s, 1H, OH) and 7.60 and 8.16 (AB system, J = 9 Hz, 4H, aromatic).

Preparation of 3,3-Dimethylpentane-2-benzoyl-4-(*p*-methylbenzoyl)di-hydrazone (4a).

A mixture of 0.01 mole of 1-phenyl-5-hydroxy-3,4,4,5-tetramethyl-2-pyrazoline (3a) and 0.012 mole of *p*-methylbenzoylhydrazine (1b) was refluxed in toluene (50 ml) of 20 hours. The residue which was left behind after evaporation of the solvent was subjected to column chromatography on silica gel (petroleum ether-ethyl acetate 1:1) to give the 3,3-dimethylpentane-2-benzoyl-4-(*p*-methylbenzoyl)dihydrazone (4a) in 39% yield (Table I); nmr (deuteriochloroform): δ 1.20 and 1.25 (two s, 6H, C(Me)₂), 1.50 and 1.92 (two s, 6H, Me), 2.35 (s, 3H, ArMe), 4.75 and 9.47 (two br s, 2H, NH), 7.05-7.90 (m, 5H, aromatic) and 7.16 and 7.71 (two d, J = 8 Hz, aromatic).

Preparation of 3,3-Dimethylpentane-2-benzoyl-4-(*p*-chlorobenzoyl)di-hydrazone (4b).

The procedure described above was followed and the 3,3-dimethylpentane-2-benzoyl-4-(*p*-chlorobenzoyl)dihydrazone was isolated in 46% yield (Table I); nmr (deuteriochloroform): δ 1.23 and 1.27 (two s, 6H, C(Me)₂), 1.48, 1.67 and 1.95 (three s, 6H, Me), 4.66 and 9.54 (two br s, 2H, NH) and 7.15-7.95 (m, 9H, aromatic).

Oxidation of bis-Aroylhydrazones 2 With Lead Tetraacetate. Formation of 1-Aroyl-5-aroylazo-3,4,4,5-tetramethyl-2-pyrazolines 6.

A general procedure (2) is described. To a solution of 0.01 mole of the bis-hydrazone 2 in methylene chloride (40 ml) a solution of 0.015 mole of lead tetraacetate in methylene chloride (40 ml) was added and the mixture was stirred at room temperature for 3 hours. The methylene chloride solution was treated with water and filtered. The organic layer was washed with sodium carbonate solution and water and then dried. The oil which was left behind after evaporation of the solvent was crystallised upon addition of a small amount of ether to give the 1-aroyl-5-aroylazo-3,4,4,5-tetramethyl-2-pyrazolines 6. Recrystallization from a mixture of ether-petroleum ether. The experimental data of the aroylazopyrazolines are given in Tables III, IV and V.

Oxidation of 3,3-Dimethylpentane-2-benzoyl-4-(*p*-methylbenzoyl)di-hydrazone (4a). Formation of 1-Benzoyl-5-(*p*-methylbenzoylazo)-3,4,4,5-tetramethyl-2-pyrazoline (7a) and 1-(*p*-Methylbenzoyl)-5-benzoylazo-3,4,4,5-tetramethyl-2-pyrazoline (8a).

The procedure described above was followed. The two isomeric pyrazolines 7a and 8a were separated with fractional crystallisation from a mixture of ether and petroleum-ether (Tables III and V).

Oxidation of 3,3-Dimethylpentane-2-benzoyl-4-(*p*-chlorobenzoyl)di-hydrazone (4b). Formation of Mixture of 1-Benzoyl-5-(*p*-chlorobenzoylazo)-3,4,4,5-tetramethyl-2-pyrazoline (7b) and 1-(*p*-chlorobenzoyl)-5-benzoylazo-3,4,4,5-tetramethyl-2-pyrazoline (8b).

Oxidation of the bis-hydrazone 4b with lead tetraacetate gave a yellow solid in 25% yield which was a mixture of the two isomeric pyrazolines

7b and 8b. All attempts to separate the two isomeric compounds with fractional recrystallisation were unsuccessful. The analytical data for the mixture are given in Table V whereas the nmr spectrum in deuteriochloroform solution and δ values is as follows: 1.10 and 1.26 (two s, 6H, C(Me)₂), 1.86 and 2.17 (two s, 6H, Me) and 7.15-8.20 (m, 9H, aromatic).

Thermal Decomposition of 1-Benzoyl-5-benzoylazo-3,4,4,5-tetramethyl-2-pyrazoline (6a).

The aroylazopyrazoline 6a 0.003 mole was refluxed in chloroform (30 ml) and the decomposition was followed by tlc. After the decomposition was complete (30 hours) the solvent was evaporated to leave behind an oil which was subjected to column chromatography (petroleum ether-ethyl acetate 7:1) to give in elution order ethyl benzoate in 74% yield, 1-benzoyl-5-methylene-3,4,4-trimethyl-2-pyrazole (10a); in 16% yield, 1-benzoyl-5-hydroxy-3,4,4,5-tetramethyl-2-pyrazoline (3a); in 3% yield and 1-benzoyl-3,4,4,5-tetramethyl-2-pyrazoline (11a) in 51% yield (for the analytical data of the decomposition products see Tables II, VI and VII).

The decomposition was repeated by refluxing in ethanol for 1 hour and the ethyl benzoate, the 1-benzoyl-5-methylene-3,4,4-trimethyl-2-pyrazole (10a) and the 1-benzoyl-3,4,4,5-tetramethyl-2-pyrazoline (11a) were isolated in 77, 27 and 31% yield, respectively.

Thermal Decomposition of 1-(*p*-Methylbenzoyl)-5-(*p*-methylbenzoylazo)-3,4,4,5-tetramethyl-2-pyrazoline (6b).

Decomposition of the aroylazopyrazoline 6b was complete by refluxing in chloroform for 60 hours. The decomposition products were separated with column chromatography (petroleum ether-ethyl acetate 9:1) in the following elution order: ethyl-*p*-toluate in 76% yield, 1-(*p*-methylbenzoyl)-5-methylene-3,4,4-trimethyl-2-pyrazole (10b) in 7% yield, 1-(*p*-methylbenzoyl)-5-hydroxy-3,4,4,5-tetramethyl-2-pyrazoline (3b) in 7% yield and 1-(*p*-methylbenzoyl)-3,4,4,5-tetramethyl-2-pyrazoline (11b) in 41% yield (Tables II, VI and VII).

Thermal Decomposition of 1-(*p*-Methoxybenzoyl)-5-(*p*-methoxybenzoylazo)-3,4,4,5-tetramethyl-2-pyrazoline (6c).

Decomposition of the aroylazopyrazoline 6c was not complete even by refluxing in chloroform for 100 hours. However, the decomposition was complete by refluxing in ethanol for 6 hours. The products were separated with column chromatography (petroleum ether-ethyl acetate 7:1) in the following elution order: ethyl-*p*-methoxybenzoate in 62% yield, 1-(*p*-methoxybenzoyl)-5-hydroxy-3,4,4,5-tetramethyl-2-pyrazoline (3c) in 31% yield and 1-(*p*-methoxybenzoyl)-3,4,4,5-tetramethyl-2-pyrazoline (11c) in 29% yield (Tables II and VII).

Thermal Decomposition of 1-(*p*-chlorobenzoyl)-5-(*p*-chlorobenzoylazo)-3,4,4,5-tetramethyl-2-pyrazoline (6d).

The decomposition products, after refluxing in chloroform for 6 hours, were separated with column chromatography (petroleum ether-ethyl acetate 7:1) and were identified as: ethyl *p*-chlorobenzoate in 60% yield, 1-(*p*-chlorobenzoyl)-5-methylene-3,4,4-trimethyl-2-pyrazoline (10b) in 48% yield and 1-(*p*-chlorobenzoyl)-3,4,4,5-tetramethyl-2-pyrazoline (11d) in 23% yield (Tables VI and VII).

Thermal Decomposition of 1-(*p*-Nitrobenzoyl)-5-(nitrobenzoylazo)-3,4,4,5-tetramethyl-2-pyrazoline (6e).

The decomposition products, after refluxing in chloroform for 6 hours, were separated with column chromatography (petroleum ether-ethyl acetate 5:1) and were identified as: ethyl *p*-nitrobenzoate in 54% yield, 1-(*p*-nitrobenzoyl)-5-hydroxy-3,4,4,5-tetramethyl-2-pyrazoline (3e) and 1-(*p*-nitrobenzoyl)-5-methylene-3,4,4-trimethyl-2-pyrazole (10e) (Tables II and VI).

Thermal Decomposition of 1-Benzoyl-5-(*p*-methylbenzoylazo)-3,4,4,5-tetramethyl-2-pyrazoline (7a).

The decomposition products, after refluxing in ethanol for 5 hours were separated with column chromatography (petroleum ether-ethyl acetate 6:1) and were identified as: ethyl *p*-toluate in 81% yield, 1-benzoyl-5-

methylene-3,4,4-trimethyl-2-pyrazole (**10a**) in 29% yield and 1-benzoyl-3,4,4,5-tetramethyl-2-pyrazoline (**11a**) in 28% yield.

Hydrolysis of 1-(*p*-Methoxybenzoyl)-5-hydroxy-3,4,4,5-tetramethyl-2-pyrazoline (**3c**).

The hydroxypyrazoline **3c** (3 g) was refluxed in concentrated hydrochloric acid (200 ml) for 10 hours. The reaction mixture was extracted repeatedly with chloroform and the combined chloroform extracts were dried and evaporated to give *p*-methoxybenzoic acid (1.4 g). The hydrochloric acid layer was made alkaline with sodium hydroxide solution and then extracted with chloroform. The organic layer was dried and evaporated to give the 3,4,4,5-tetramethyl-4*H*-pyrazole (**5**) (1.2 g) in 89% yield, mp 48-50° (lit (9) mp 51°).

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