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Reactions of 2-chloroformylhydrazones of aromatic aldehydes or ketones **2** with various hydrazines were converted to monocarbonohydrazone derivatives **3** or **5** and/or tetrahydro-1,2,4,5-tetrazin-3(2H)-one derivatives **6**, **7**. By oxidation with lead dioxide, compounds **6** were transformed into stable 3,4-dihydro-3-oxo-1,2,4,5-tetrazin-1(2H)-yl radical derivatives **8**.

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Reactions of 2-chloroformylhydrazones of aromatic aldehydes or ketones **2** with hydrazine hydrate and aryl, benzyl or alkylhydrazines have been investigated. New 2-chloroformylhydrazones **2** were prepared in good yields by treatment of the corresponding hydrazones **1** with phosgene in the presence of pyridine as reported in recent papers for **2a,e,i** [1]. They are presented in Table I.

As expected, the reaction of **2a** with hydrazine hydrate in ethanol were converted exclusively into the corresponding monocarbonohydrazone **3a** [1b]. By action of benzaldehyde, the dicarbonohydrazone **4** was formed [1b]. In contrast to the results reported by Busch and Walter [2] for phenylhydrazine and Raphaelian, *et al.* [3] for methylhydrazine, reactions of compounds **2** with these hydrazines provided, in addition to the monocarbonohydrazone **3** as indicated by the authors, the corresponding isomeric tetrahydro-1,2,4,5-tetrazin-3(2H)-ones **6** (Scheme 1).

The reactions proceeded by 1-*N*- and/or 2-*N*-acylations of substituted hydrazines, giving monocarbonohydrazone **3** and/or **5**. As expected, the compound **3**/compound **5**

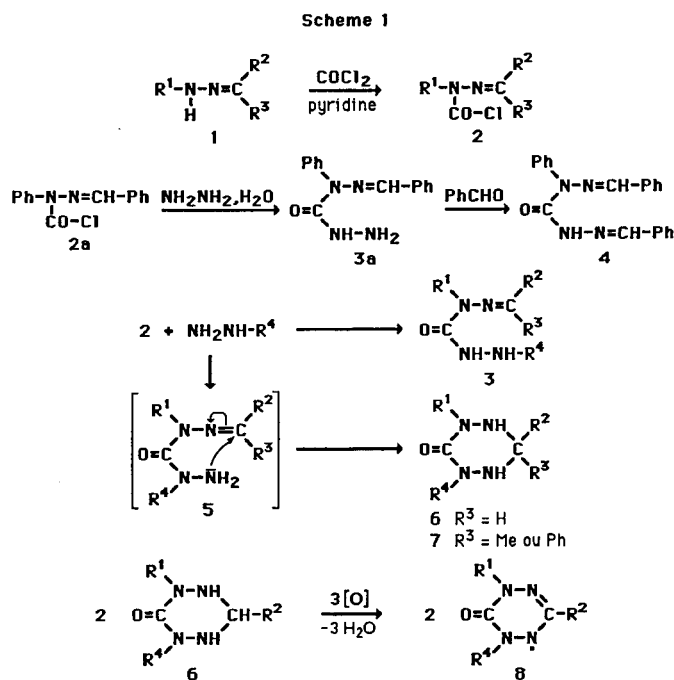


Table I

2	R ¹	R ²	R ³	Yield %[a]	Mp °C	Formula	M.W.	Analyses, %			IR, ν cm ⁻¹	
								Calcd.	Found			
								C	H	N		
a	Ph	Ph	H	91	102 [b,c]	C ₁₄ H ₁₁ ClN ₂ O						1720, 1590
b	Ph	4-MeOPh	H	78	92 [d,e]	C ₁₅ H ₁₃ ClN ₂ O ₂	288.72	62.40 (62.48)	4.54 (4.51)	9.70 (9.77)		1730, 1600
c	Ph	4-NO ₂ Ph	H	95	136 [b,f]	C ₁₄ H ₁₀ ClN ₂ O ₃	303.69	55.36 (55.48)	3.32 (3.36)	13.84 (13.67)		1725, 1585
d	Ph	4-MeOCOPh	H	83	149 [b,f]	C ₁₆ H ₁₃ ClN ₂ O ₃	316.73	60.67 (60.83)	4.14 (4.11)	8.84 (8.83)		1720 (b), 1590
e	Ph	4-ClPh	H	75	85 [b,g]	C ₁₄ H ₁₀ Cl ₂ N ₂ O						1720, 1590
f	Ph	2,4-diClPh	H	80	116 [b,f]	C ₁₄ H ₉ Cl ₂ N ₂ O	327.59	51.33 (51.44)	2.77 (2.78)	8.55 (8.45)		1720, 1585
g	4-MePh	Ph	H	62	116 [b]	C ₁₅ H ₁₃ ClN ₂ O	272.72	66.06 (66.20)	4.80 (4.82)	10.27 (10.22)		1720, 1600
h	4-NO ₂ Ph	Ph	H	81	168 [b]	C ₁₄ H ₁₀ ClN ₂ O ₃	303.69	55.36 (55.27)	3.32 (3.28)	13.84 (13.85)		1730, 1600
i	Me	Ph	H	75	88 [b,h]	C ₉ H ₉ ClN ₂ O						1710, 1600
j	Ph	Ph	Me	82	86 [b]	C ₁₅ H ₁₃ ClN ₂ O	272.72	66.06 (66.09)	4.80 (4.84)	10.27 (10.37)		1725, 1590
k	Ph	Ph	Ph	65	58 [d,e]	C ₂₀ H ₁₅ ClN ₂ O	334.79	71.75 (71.80)	4.52 (4.41)	8.37 (8.33)		1680, 1590

[a] Non optimized yields with methods A or B. [b] Cyclohexane. [c] Lit [2] mp 101-102°. [d] Diethyl ether. [e] Petroleum ether 40-60. [f] Benzene.

[g] Lit [1a] was first presented as an indistillable oil. [h] Lit [3] mp 88°.

Table II
 Monocarbonohydrazones **3**

3	R ¹	R ²	R ³	R ⁴	[a]	Yield % [b]	Mp °C	Formula	Analyses, %			IR, ν cm ⁻¹	¹ H NMR [c] δ ppm
									Calcd./Found	C	H		
a	Ph	Ph	H	H	-	76	202 [d,e]	C ₁₄ H ₁₄ N ₄ O					
b	Ph	Ph	H	Ph	6a	15	178 [f]	C ₂₀ H ₁₈ N ₄ O (330.37)	72.71 72.69	5.49 5.46	16.96 16.97	3420, 3300, 1675, 1595	6.5-7.8 (m, 17H), 9.4 (s, 1H)
c	Ph	Ph	H	4-MeOPh	6c	12	196 [f]	C ₂₁ H ₂₀ N ₄ O ₂ (360.40)	69.98 69.92	5.59 5.67	15.55 15.50	3430, 3240, 1680, 1600	3.75 (s, 3H), 6.6-7.8 (m, 16H), 9.4 (s, 1H)
d	Ph	Ph	H	4-NO ₂ Ph	-	70	224 [f]	C ₂₀ H ₁₇ N ₅ O ₃ (375.37)	63.99 64.16	4.57 4.60	18.66 18.54	3400, 3260, 1660, 1600	6.8 and 8 (2d, 4H), 7-7.8 (m, 11H), 8.9 (s, 1H), 9.7 (s, 1H)
e	Ph	Ph	H	<i>i</i> -Bu	-	48	152 [g]	C ₁₈ H ₂₂ N ₄ O (310.38)	69.65 69.46	7.14 7.10	18.05 18.20	3400, 3300, 1675, 1600	1.15 (s, 9H), 4.75 (s, 1H), 7.25-8 (m, 11H), 8.75 (s, 1H)
f	Ph	4-MeOPh	H	4-NO ₂ Ph	-	73	192 [h]	C ₂₁ H ₁₉ N ₅ O ₄ (405.40)	62.21 62.18	4.72 4.77	17.28 17.24	3300, 3200, 1660, 1600	3.8 (s, 3H), 6.9-8.3 (m, 14H), 9.2 (s, 1H), 9.95 (s, 1H)
g	Ph	4-NO ₂ Ph	H	CH ₂ CO ₂ Et	6x	20	203 [i]	C ₁₈ H ₁₉ N ₅ O ₅ (385.37)	56.10 56.11	4.97 4.97	18.17 18.01	3300, 3200, 1750, 1670, 1575	1.2 (t, 3H), 3.7 (s, 2H), 4.2 (q, 2H), 5.1 (s, 1H), 7.2-8.4 (m, 10H), 9.2 (s, 1H)
h	Ph	Ph	Ph	Ph	7d	47	220 [j]	C ₂₆ H ₂₂ N ₄ O (406.46)	76.82 77.15	5.46 5.49	13.78 13.66	3370, 3300, 1685, 1600	6.7-7.8 (m, 21H), 9 (s, 1H)

[a] Tetrazinones **6** or **7** obtained besides the corresponding monocarbonohydrazone **3**. [b] Non optimized yields. [c] In DMSO-*d*₆. [d] Methanol. [e] Lit [1b] mp 202°. [f] *i*-Propanol. [g] Cyclohexane. [h] Ethanol. [i] Ethyl acetate. [j] Benzene.

molar ratio was dependent on the electronic effects of the substituents borne by the hydrazine derivatives. Generally, with methylhydrazine, ethyl hydrazinoacetate, 3-hydrazinopropionitrile, benzylhydrazine or arylhydrazines for which the aryl substituents were electron-donating groups, compounds **5** were formed. But they were not isolated because they cyclized immediately by intramolecular addition reaction of the NH₂ group with the hydrazone C=N imino group to give tetrahydro-tetrazinones **6** in good yields.

Reactions occurred in various solvents such as ethanol, benzene, dichloromethane or dimethylformamide, often at room temperature in the presence of an excess of hydrazine derivatives and sometimes in the presence of pyridine (see Experimental). Most of these reactions were exothermic and their duration was variable from a few minutes to half an hour. With *tert*-butylhydrazine, the steric hindrance of the substituent was a more important factor than the electronic effect, with orientation of the reaction towards monocarbonohydrazone **3e**.

In the literature, a similar but reversible ring formation was reported for monothiocarbonohydrazone, homologous to the intermediate **5**, which gave tetrahydro-1,2,4,5-tetrazine-3(2*H*)-thione besides other heterocycles [4,5].

When a mixture of compounds **3** and **6** was obtained, the separation of **6** was effected by recrystallization. Compounds **3** were obtained by evaporation of the filtrate and further recrystallization or column chromatography. Compounds **3** and **6** are listed in Tables II and III, respectively.

Under the same conditions, reaction of some methyl(or aryl)hydrazines with the chloroformylhydrazone of acetophenone, **2j** or benzophenone, **2k** afforded tetrazinones **7** (Table IV).

Attempts to prepare thio analogues of tetrazinones **6** from chlorothioformylhydrazones were unsuccessful. Resinous mixtures were formed by treatment of hydrazones **1** with thiophosgene.

Oxidation of tetrahydro-tetrazinones **6** with lead dioxide into stable 3,4-dihydro-3-oxo-1,2,4,5-tetrazin-1(2*H*)-yl radicals **8** were performed in dichloromethane in the presence of acetic acid. Many other oxidants as K₃Fe(CN)₆ [6], Ag₂CO₃, H₂O₂, ThO₂, MnO₂ could be used. The new 2,4,6-triaryl substituted radicals **8a-m** were obtained in very good yields as purple and well crystallized compounds with melting points above 140° (Table V). They were particularly stable compounds. No transformation of these compounds was observed after storage at room temperature for one year. Radicals bearing alkyl or benzyl groups **8n-aa** were also formed from tetrazinones **6**, as indicated by a strong red coloration after addition of the oxidant to the corresponding tetrazinones **6** solutions. But their low stability and particularly the difficulty to obtain them in very pure state have not permitted their inclusion in Table V, except for **8s**, and also for **8aa** which was obtained from **6aa** by the same method [6a,7].

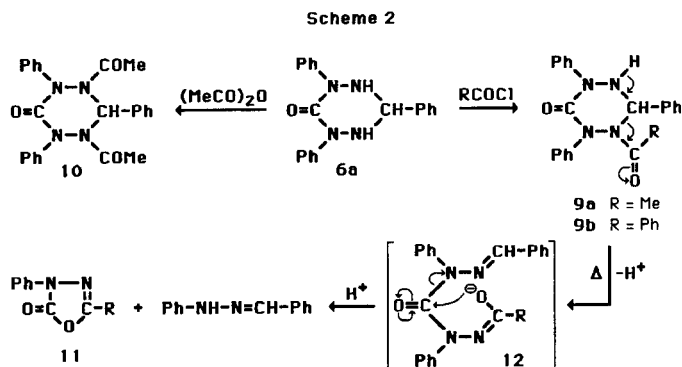


Table III

Tetrahydro-1,2,4,5-tetrazin-3(2H)-ones 6											
6	R ¹	R ²	R ⁴	Yield % ^[a]	Mp °C	Formula	Analyses, % Calcd./Found			IR, ν cm ⁻¹	¹ H NMR [b] δ ppm
							C	H	N		
a	Ph	Ph	Ph	69	220 [c]	C ₂₀ H ₁₈ N ₄ O (330.37)	72.71 72.90	5.49 5.49	16.96 16.84	3230, 3210, 1620, 1600	5.3 (t, 1H, J = 8 Hz), 6.3 (2d, 2H), 6.9-7.6 (m, 15H)
b	Ph	4-MeOPh	Ph	56	216 [c]	C ₂₁ H ₂₀ N ₄ O ₂ (360.40)	69.98 69.81	5.59 5.59	15.55 15.59	3230, 3210, 1615, 1590	3.75 (s, 3H), 5.35 (t, 1H, J = 9 Hz), 6.35 (2d, 2H), 6.9-7.8 (m, 14H)
c	Ph	4-NO ₂ Ph	Ph	92	226 [c]	C ₂₀ H ₁₇ N ₅ O ₃ (375.37)	63.99 64.00	4.57 4.58	18.66 18.50	3220, 1620, 1600	5.6 (t, 1H, J = 8 Hz), 6.7 (2d, 2H), 7.2-8.4 (m, 14H)
d	Ph	4-MeOCOPh	Ph	31	270 [d]	C ₂₂ H ₂₀ N ₄ O ₃ (388.41)	68.03 68.03	5.19 5.26	14.43 14.30	3230, 3210, 1720, 1620	3.85 (s, 3H), 5.45 (t, 1H, J = 9 Hz), 6.5 (2d, 2H), 7-8.05 (m, 14H)
e	Ph	4-ClPh	Ph	52	230 [e]	C ₂₀ H ₁₇ ClN ₄ O (364.82)	65.84 65.67	4.70 4.72	15.36 15.38	3220, 1615, 1590	5.45 (t, 1H, J = 9 Hz), 6.5 (2d, 2H), 6.7-7.7 (m, 12H), 7.95 (d, 2H)
f	Ph	2,4-diClPh	Ph	77	197 [e]	C ₂₀ H ₁₆ Cl ₂ N ₄ O (399.26)	60.16 60.33	4.04 4.07	14.03 13.94	3250, 1630, 1615	5.6 (t, 1H), 6.6 (2d, 2H), 7-7.85 (m, 13H)
g	Ph	Ph	4-MePh	58	187 [c]	C ₂₁ H ₂₀ N ₄ O (344.40)	73.23 73.14	5.85 5.86	16.27 16.34	3230, 1620, 1610	2.3 (s, 3H), 5.35 (t, 1H, J = 8 Hz), 6.3 (2d, 2H), 7-7.7 (m, 14H)
h	Ph	4-MeOPh	4-MePh	60	202 [f,g]	C ₂₂ H ₂₂ N ₄ O ₂ (374.42)	70.57 70.51	5.92 5.98	14.96 14.93	3240, 1630, 1610	2.3 (s, 3H), 3.8 (s, 3H), 5.35 (t, 1H, J = 9 Hz), 6.35 (2d, 2H), 6.9-7.8 (m, 13H)
i	Ph	4-NO ₂ Ph	4-MePh	77	238 [h]	C ₂₁ H ₁₉ N ₅ O ₃ (389.40)	64.77 64.77	4.92 4.86	17.99 17.87	3230, 3220, 1620, 1600	2.3 (s, 3H), 5.65 (t, 1H, J = 9 Hz), 6.65 (2d, 2H), 7.15-8.4 (m, 13H)
j	Ph	Ph	4-MeOPh	55	162 [c,i]	C ₂₁ H ₂₀ N ₄ O ₂ (360.40)	69.98 70.16	5.59 5.64	15.55 15.71	3240, 3200, 1620, 1610	3.75 (s, 3H), 5.4 (t, 1H, J = 9 Hz), 6.35 (2d, 2H), 6.85-7.7 (m, 14H)
k	Ph	4-MeOPh	4-MeOPh	66	163 [c]	C ₂₂ H ₂₂ N ₄ O ₃ (390.42)	67.68 67.68	5.68 5.72	14.35 14.30	3250, 3230, 1610, 1580	3.75 (2s, 6H), 5.3 (t, 1H, J = 9 Hz), 6.35 (2d, 2H), 6.9-7.8 (m, 13H)
l	Ph	4-NO ₂ Ph	4-MeOPh	79	211 [d]	C ₂₁ H ₁₉ N ₅ O ₄ (405.40)	62.21 62.35	4.72 4.77	17.28 17.14	3240, 3230, 1630, 1605	3.8 (s, 3H), 5.6 (t, 1H, J = 8 Hz), 6.65 (2d, 2H), 7-8.5 (m, 13H)
m	4-NO ₂ Ph	Ph	Ph	85	192 [c]	C ₂₀ H ₁₇ N ₅ O ₃ (375.37)	63.99 63.94	4.57 4.59	18.66 18.63	3240, 1625, 1595	5.4 (t, 1H, J = 9 Hz), 6.5 (d, 1H), 6.6 (d, 1H), 7.05-7.7 (m, 10H), 7.85 and 8.2 (2d, 4H)
n	Ph	Ph	CH ₂ Ph	45	132 [c]	C ₂₁ H ₂₀ N ₄ O (344.40)	73.23 73.15	5.85 5.82	16.27 16.31	3240, 3220, 1615, 1585	4.6 and 4.9 (2d, 2H, J = 16 Hz), 5.15 (t, 1H, J = 8 Hz), 5.9 (d, 1H), 6.3 (d, 1H), 7-7.9 (m, 15H)
o	Ph	4-MeOPh	CH ₂ Ph	71	168 [c]	C ₂₂ H ₂₂ N ₄ O ₂ (374.42)	70.57 70.60	5.92 5.88	14.96 15.06	3240, 3200, 1615, 1585	3.75 (s, 3H), 4.6 and 4.9 (2d, 2H, J = 16 Hz), 5.05 (t, 1H, J = 9 Hz), 5.8 (d, 1H), 6.2 (d, 1H), 6.9-7.85 (m, 14H)
p	Ph	Ph	Me	52	119 [e]	C ₁₅ H ₁₆ N ₄ O (268.31)	67.14 67.21	6.01 6.00	20.88 20.75	3250, 3230, 1610	3.1 (s, 3H), 5.15 (t, 1H, J = 9 Hz), 5.9 (d, 1H), 6.15 (d, 1H), 6.9-7.7 (m, 10H)
q	Ph	4-MeOPh	Me	56	140 [f,g]	C ₁₆ H ₁₈ N ₄ O ₂ (298.33)	64.41 64.49	6.08 6.09	18.78 18.88	3240, 3200, 1610, 1585	3.05 (s, 3H), 3.7 (s, 3H), 5.05 (t, 1H, J = 9 Hz), 5.8 (d, 1H), 6.1 (d, 1H), 6.85-7.8 (m, 9H)
r	Ph	4-NO ₂ Ph	Me	61	140 [c]	C ₁₅ H ₁₅ N ₅ O ₃ (313.31)	57.50 57.60	4.83 4.88	22.35 22.19	3240, 1630, 1610	3.1 (s, 3H), 5.4 (t, 1H, J = 8 Hz), 6.1 (d, 1H), 6.4 (d, 1H), 6.95-7.7 (m, 5H), 7.85 and 8.25 (2d, 4H)
s	Ph	4-MeOCOPh	Me	72	180 [c]	C ₁₇ H ₁₈ N ₄ O ₃ (326.34)	62.56 62.31	5.56 5.61	17.17 16.98	3220, 3210, 1710, 1630, 1610	3.1 (s, 3H), 3.85 (s, 3H), 5.3 (m, 1H), 5.9 (m, 1H), 6.25 (d, 1H), 6.9-8.1 (m, 9H)
t	Ph	4-ClPh	Me	52	150 [f,g]	C ₁₅ H ₁₅ ClN ₄ O (302.75)	59.50 59.39	4.99 4.95	18.51 18.41	3220, 3195, 1630, 1590	3.1 (s, 3H), 5.2 (t, 1H, J = 8 Hz), 5.95 (d, 1H), 6.2 (d, 1H), 7-7.7 (m, 9H)
u	Ph	2,4-diClPh	Me	61	152 [e]	C ₁₅ H ₁₄ Cl ₂ N ₄ O (337.20)	53.43 53.81	4.19 4.26	16.62 16.47	3270, 3230, 1600, 1590	3.1 (s, 3H), 5.3 (t, 1H, J = 9 Hz), 6.15 (d, 1H), 6.3 (d, 1H), 7-7.7 (m, 8H)
v	4-NO ₂ Ph	Ph	Me	47	200 [c]	C ₁₅ H ₁₅ N ₅ O ₃ (313.31)	57.50 57.52	4.83 4.78	22.35 22.36	3230, 1620, 1600	3.1 (s, 3H), 5.2 (t, 1H, J = 9 Hz), 6.1 (d, 1H), 6.4 (d, 1H), 7.25-7.6 (m, 5H), 7.95 and 8.15 (2d, 4H)
w	Ph	Ph	CH ₂ CO ₂ Et	65	88 [e,j]	C ₁₈ H ₂₀ N ₄ O ₃ (340.37)	63.51 63.80	5.92 5.89	16.46 16.32	3240, 3200, 1740, 1640, 1620	1.2 (t, 3H), 4.05 and 4.5 (2d, 2H, J = 17 Hz), 4.15 (q, 2H), 5.2 (t, 1H, J = 10 Hz), 5.95 (d, 1H), 6.3 (d, 1H), 7.05-7.75 (m, 10H)
x	Ph	4-NO ₂ Ph	CH ₂ CO ₂ Et	45	137 [k,l]	C ₁₈ H ₁₉ N ₅ O ₅ (385.37)	56.10 55.97	4.97 4.93	18.17 18.18	3260, 3240, 1740, 1615	1.2 (t, 3H), 4.05 and 4.5 (2d, 2H, J = 17 Hz), 4.15 (q, 2H), 5.4 (t, 1H, J = 10 Hz), 6.15 (d, 1H), 6.55 (d, 1H), 7-8.3 (m, 9H)
y	Ph	Ph	(CH ₂) ₂ CN	57	134 [f,g]	C ₁₇ H ₁₇ N ₅ O (307.34)	66.43 66.60	5.58 5.60	22.79 22.69	3220, 3170, 2220, 1605, 1580	2.8 (t, 2H), 3.4-4.1 (m, 2H), 5.15 (t, 1H, J = 10 Hz), 5.85 (d, 1H), 6.2 (d, 1H), 7-7.7 (m, 10H)
z	Ph	4-MeOPh	(CH ₂) ₂ CN	53	137 [e]	C ₁₈ H ₁₉ N ₅ O ₂ (337.37)	64.08 64.30	5.68 5.65	20.76 20.71	3240, 3220, 2240, 1630, 1590	2.8 (t, 2H), 3.4-4.1 (m, 2H), 3.75 (s, 3H), 5.1 (t, 1H, J = 10 Hz), 5.8 (d, 1H), 6.15 (d, 1H), 6.9-7.75 (m, 9H)
aa	Me	Ph	Me	73	139 [j,m]	C ₁₀ H ₁₄ N ₄ O			3240, 3200, 1590 (b)		

[a] Non optimized yields. [b] In DMSO-d₆. [c] 1-Propanol. [d] Butyl acetate. [e] Ethanol. [f] Cyclohexane. [g] Benzene. [h] 1-Butanol [i] This compound was also prepared from chloroformylhydrazone 1g with phenylhydrazine, yield 58 %. [j] Water. [k] Ethyl acetate. [l] Petroleum ether 40-60. [m] Lit [6] mp 138-139°.

Table IV
Tetrahydro-1,2,4,5-tetrazin-3(2H)-ones 7

7	R ¹	R ²	R ³	R ⁴	Yield %[a]	Mp °C	Formula	Analyses, % Calcd./Found C H N	IR, ν cm ⁻¹	¹ H NMR [b] δ ppm
a	Ph	Ph	Me	Ph	25	185 [c]	C ₂₁ H ₂₀ N ₄ O (344.40)	73.23 5.85 16.27 72.86 5.87 16.45	3250, 3230 1630, 1600	1.45 (s, 3H), 6.3 (2s, 2H), 7-7.7 (m, 15H)
b	Ph	Ph	Me	4-MePh	31	169 [d]	C ₂₂ H ₂₂ N ₄ O (358.42)	73.72 6.19 15.63 73.58 6.24 15.81	3260, 3230 1630	1.45 (s, 3H), 2.3 (s, 3H), 6.3 (2s, 2H), 7-7.7 (m, 14H)
c	Ph	Ph	Me	Me	85	146 [e, f]	C ₁₆ H ₁₈ N ₄ O (282.33)	68.06 6.43 19.84 68.16 6.51 19.87	3240, 3210 1615, 1590	1.4 (s, 3H), 3.05 (s, 3H), 5.85 (s, 1H), 6.15 (s, 1H), 6.9-7.7 (m, 10H)
d	Ph	Ph	Ph	Ph	21	250 [g]	C ₂₆ H ₂₂ N ₄ O (406.46)	76.82 5.46 13.78 76.47 5.42 13.68	3300, 3230 1640, 1595	6.7 (2s, 2H), 7.1-7.8 (m, 20H)
e	Ph	Ph	Ph	Me	80	200 [c]	C ₂₁ H ₂₀ N ₄ O (344.40)	73.23 5.85 16.27 73.22 5.81 16.38	3240, 1615 1595	3.15 (s, 3H), 6.2 (s, 1H), 6.55 (s, 1H), 7.2-7.85 (m, 15H)

[a] Non optimized yields. [b] In DMSO-d₆. [c] 1-Propanol. [d] 1-Butanol. [e] Cyclohexane. [f] Benzene. [g] Ethanol.

Table V
3,4-Dihydro-3-oxo-1,2,4,5-tetrazin-1(2H)-yl Radicals 8

8	R ¹	R ²	R ⁴	Yield %[a]	Mp °C [b]	Formula	M.W.	Analyses, % Calcd.(Found)			IR, ν cm ⁻¹
								C	H	N	
a	Ph	Ph	Ph	70	210	C ₂₀ H ₁₅ N ₄ O	327.35	73.38 (73.37)	4.62 (4.68)	17.12 (17.00)	1690, 1590
b	Ph	4-MeOPh	Ph	83	168	C ₂₁ H ₁₇ N ₄ O ₂	357.37	70.57 (70.49)	4.79 (4.86)	15.68 (15.52)	1685, 1605, 1595
c	Ph	4-NO ₂ Ph	Ph	75	262	C ₂₀ H ₁₄ N ₄ O ₃	372.35	64.51 (64.25)	3.79 (3.80)	18.81 (18.77)	1690, 1605, 1590
d	Ph	4-MeOCOPh	Ph	71	230	C ₂₂ H ₁₇ N ₄ O ₃	385.38	68.56 (68.42)	4.45 (4.49)	14.54 (14.47)	1720, 1690, 1610, 1590
e	Ph	4-ClPh	Ph	78	220	C ₂₀ H ₁₄ ClN ₄ O	361.79	66.39 (66.29)	3.90 (3.89)	15.49 (15.42)	1690, 1590
f	Ph	2,4-diClPh	Ph	81	140	C ₂₀ H ₁₃ Cl ₂ N ₄ O	396.24	60.62 (60.80)	3.31 (3.34)	14.14 (14.07)	1695, 1630, 1590
g	Ph	Ph	4-MePh	81	188	C ₂₁ H ₁₇ N ₄ O	341.37	73.88 (73.81)	5.02 (5.06)	16.41 (16.45)	1690, 1595
h	Ph	4-MeOPh	4-MePh	78	167	C ₂₂ H ₁₉ N ₄ O ₂	371.40	71.14 (71.17)	5.16 (5.21)	15.09 (15.02)	1690, 1610
i	Ph	4-NO ₂ Ph	4-MePh	83	249	C ₂₁ H ₁₆ N ₄ O ₃	386.37	65.28 (65.25)	4.17 (4.22)	18.13 (18.26)	1690, 1600
j	Ph	Ph	4-MeOPh	79	159	C ₂₁ H ₁₇ N ₄ O ₂	357.37	70.57 (70.59)	4.79 (4.86)	15.68 (15.68)	1685, 1605, 1595
k	Ph	4-MeOPh	4-MeOPh	75	148	C ₂₂ H ₁₉ N ₄ O ₃	387.40	68.20 (68.35)	4.94 (5.02)	14.46 (14.39)	1685, 1605, 1595
l	Ph	4-NO ₂ Ph	4-MeOPh	76	220	C ₂₁ H ₁₆ N ₄ O ₄	402.37	62.68 (62.52)	4.01 (4.08)	17.41 (17.28)	1700, 1605, 1595
m	4-NO ₂ Ph	Ph	Ph	72	246	C ₂₀ H ₁₄ N ₄ O ₃	372.35	64.51 (64.59)	3.79 (3.78)	18.81 (18.74)	1690, 1605, 1590
s	Ph	4-MeOCOPh	Me	35	160 [c]	C ₁₇ H ₁₅ N ₄ O ₃	323.32	63.15 (63.01)	4.68 (4.72)	17.33 (17.41)	1715, 1690, 1610, 1590
aa	Me	Ph	Me	80	73 [d]	C ₂₀ H ₁₅ N ₄ O					

[a] Non optimized yields with methods A or B. [b] Tetrazin-1(2H)-yl radicals 8 were recrystallized in cyclohexane or in diethyl ether/petroleum ether 40-60.
[c] This compound sublimated at its melting point. [d] Lit [6a,7] mp 73°.

Table VI

Hyperfine Coupling Constants in Gauss Used for Simulation of Radicals 8h,s

8	R ¹	R ²	R ⁴	a _{N1}	a _{N2}	a _{N4}	a _{N5}	a _H (R ⁴)	band width
h	Ph	4-MeOPh	4-MePh	4.60	6.30	6.30	4.60	-	4
s	Ph	4-MeOCOPh	Me	5.80	5.80	5.80	5.35	4.90	4

A preceding synthesis of tetrazinones **6** was effected by the action of aldehydes with the symmetrical 2,4-dimethyl(or dibenzyl)carbonohydrazide, obtained from the reaction of phosgene with 2-methyl(or benzyl)hydrazide of benzaldehyde, followed by acid hydrolysis [6]; this synthesis was of limited scope. The synthesis reported here is more general, but one limitation exists for the preparation of radicals **8** which bear two electron-withdrawing groups at positions 2 and 4 of the heterocycle. The synthesis of compounds **6** with only one electron-withdrawing group at position 2 or 4 of the heterocycle must be obtained from the chloroformylhydrazide **2** bearing this group.

Monoacyl derivatives of **6a**, compounds **9** and a diacetyl derivative of **6a**, compound **10**, have been prepared by classical methods (Scheme 2). When **9a** or **9b**, monoacetyl or monobenzoyl derivatives of **6a**, respectively, were heated for a few minutes at their melting points, they were decomposed into benzaldehyde phenylhydrazone and 5-methyl-3-phenyl(or 3,5-diphenyl)-1,3,4-oxadiazol-2(3H)-ones **11a,b**.

This result could be explained by a possible ionic mechanism. By heating, ring opening of **9** into **12** would be followed by an intramolecular attack of the resulting iminoalcoholate ion at the carbonyl group. However, since this reaction is a thermal decomposition, a radical reaction mechanism should not be eliminated.

Assignment for the structures of new products was verified by elemental analysis, ir and ¹H-nmr or esr spectra.

The esr spectra of radicals **8** in a solution of dichloromethane are very similar for all compounds with three

phenyl ring substituents. They show nine broadened lines which are consistent with the interaction of the unpaired electron with four non-equivalent nitrogen atoms. Dilution and utilization of other solvents (cyclohexane, tetrahydrofuran) did not alter significantly the esr spectra. This behaviour is consistent with line-broadening due to small proton hyperfine coupling constants on the phenyl rings. There is no evidence for Heisenberg spin exchange as observed on similar radicals [8]. The methyl substituted radical **8s** gives a twelve line spectrum due to the additional hyperfine coupling constant of the methyl group. The determination of the coupling constants were carried out for a triphenyl radical **8h** and for the methyl radical **8s**. Simulations were performed according to Oehler and Janzen [9] using a large line width including the small hyperfine coupling constants. Hyperfine coupling constants for nitrogen a_N and hydrogen a_H (CH_3) are summarized in Table VI. The tentative assignments of $a_{N,2,4}$ and $a_{N,1,5}$ couplings were made by comparison with similar products [7].

EXPERIMENTAL

Melting points (uncorrected) were determined with a Büchi oil heated apparatus. The ir spectra were recorded on a Perkin Elmer 1310 spectrophotometer as potassium bromide disks. The ^1H -nmr spectra were obtained in DMSO-d_6 on a Bruker WP 80 spectrometer and are reported as δ values (ppm) relative to tetramethylsilane as an internal standard. The esr spectra were recorded on a Varian E-109 spectrometer operating at 9.5 GHz with a 100 kHz modulation. The sample solutions were examined in a flat quartz cell inserted in an E-238 cavity operating in the TM_{110} mode. To avoid saturation effects, microwave power was adjusted to 10 mW and radical concentrations were fixed to 2 mM.

2-Chloroformylarylhyazones of Aromatic Aldehydes, **2a-i** and of Ketones, **2j,k**.

Compounds **2a,e,i** were previously described [1-3]. All compounds **2** were prepared by a modified procedure. To a fresh and stirred solution of 1.24 g (12.5 mmoles) of phosgene in 15 ml of dry toluene was added, dropwise at 0° , a solution of 10 mmoles of arylhydrazone of aromatic aldehyde or ketone and 0.87 g (11 mmoles) of dry pyridine in dry ethyl acetate/benzene (1/1). The volume was a function of the hydrazone solubility. After complete addition, the mixture was heated at $60\text{--}80^\circ$ for 45 minutes, then filtered. Solvents were evaporated in a hood and the crude product **2** was recrystallized twice from a suitable solvent (Table I).

1-Benzylidene-2-phenylcarbonohydrazone (**3a**) and 1,4-Dibenzylidene-2-phenylcarbonohydrazone (**4**).

To a stirred solution of 1.5 g (30 mmoles) of hydrazine hydrate in 50 ml of ethanol, was added in small portions at room temperature, 2.58 g (10 mmoles) of chloroformylhydrazone **2a**. A few minutes later, white crystals separated. After 15 minutes, ethanol was evaporated and the resulting crop **3a** was recrystallized from methanol (Table II). Compound **4** was obtained in quantitative yield by treatment of **3a** with benzaldehyde in hot ethanol. It was recrystallized from ethyl acetate, mp 192° , lit [1b] mp 192° .

Tetrahydro-1,2,4,5-tetrazin-3(2*H*)-ones **6,7** and/or 2,4-Disubstituted 1-Arylidene-carbonohydrizides **3b-h**.

To a stirred solution of 20 mmoles of aryl, benzyl or alkylhydrazone in 50 ml of ethanol was added, at room temperature in small portions, 10 mmoles of chloroformylhydrazone **2a-i**. In most cases, the reaction occurred quickly and was exothermic. Often after a few minutes, a part of tetrazinone **6** precipitated. However, the reaction mixture was stirred for 30 minutes at $40\text{--}60^\circ$. After cooling, it was poured onto 150 ml of ice-water. Tetrazinone **6** and/or monocarbonohydrazone **3** precipitated. When tetrazinone **6** was formed, it was easily purified from compound **3** by two recrystallizations from a suitable solvent (Table III). If compound **3** was also present, it was isolated by evaporation of the recrystallization filtrate of **6** and was purified by recrystallization from a suitable solvent or by chromatographic techniques (Table II). In two cases, **6p** and **6aa** chloroformylhydrazone **2** was added as a solution in a minimum amount of dichloromethane to the ethanolic solution of the hydrazine derivative. By this procedure, compounds **3** and **6** were isolated by extraction with dichloromethane after pouring the reaction mixture into ice-water. When 4-nitrophenylhydrazone was used (compounds **3d,f**), 10 mmoles of chloroformylhydrazone **2** were added to a solution of 10 mmoles of hydrazine and 10 mmoles of pyridine in a mixture of 40 ml of ethanol and the minimum volume of DMF for solution. The reaction mixture was heated at 80° for 10 minutes. Lastly, reactions of 10 mmoles of the hydrazines with chloroformylhydrazones of acetophenone, **2j** and benzophenone, **2k** (10 mmoles in a minimum amount of dichloromethane) were accomplished in 50 ml of dry benzene, in the presence of 0.87 g (11 mmoles) of pyridine to give tetrazinones **7** (Table IV).

3,4-Dihydro-3-oxo-1,2,4,5-tetrazin-1(2*H*)-yl Radicals **8**.

To a stirred solution of 1 mmole of tetrazinone **6** in 10 ml of dichloromethane and 1 ml of acetic acid, was added in small portions 0.29 g (1.2 mmoles) of lead dioxide over 15 minutes. A strong purple or red coloration appeared. The reaction mixture was heated to $30\text{--}40^\circ$ for a few minutes. After filtration, the filtrate was washed with water until it was neutral. The organic layer was dried over magnesium sulfate, then evaporated. The colored crop **8** was recrystallized from a suitable solvent (Table V). Many radicals bearing an alkyl or a benzyl group, **8n-r**, **t-aa**, were not obtained in a pure state after several recrystallizations.

Tetrahydro-1-acetyl-2,4,6-triphenyl-1,2,4,5-tetrazin-3(2*H*)-one (**9a**).

To a stirred solution of 3.3 g (10 mmoles) of tetrazinone **6a** and 0.78 g (10 mmoles) of acetyl chloride in 50 ml of dry ethyl acetate, was added 1 g (12 mmoles) of sodium bicarbonate. The mixture was refluxed for 3 hours, then the solvent was evaporated. To the resulting crop was added 50 ml of ice-water. The insoluble compound was filtered and washed with 50 ml of water, then dried and recrystallized from ethyl acetate giving 2.8 g of **9a** (75%), mp 180° ; ir: 3310, 1680, 1675, 1590 cm^{-1} ; ^1H -nmr (DMSO-d_6): δ 1.95 (s, 3H), 7.2-7.8 (m, 16H), 10.55 (s, 1H).

Anal. Calcd. for $\text{C}_{22}\text{H}_{20}\text{N}_4\text{O}_2$ (372.41): C, 70.95; H, 5.41; N, 15.04. Found: C, 70.54; H, 5.41; N, 15.04.

Tetrahydro-1-benzoyl-2,4,6-triphenyl-1,2,4,5-tetrazin-3(2*H*)-one (**9b**).

A mixture of 0.66 g (2 mmoles) of tetrazinone **6a**, 0.2 g (2.4 mmoles) of sodium bicarbonate and 0.28 g (2 mmoles) of benzoyl

chloride in 30 ml of dry ethyl acetate was stirred at reflux for 90 minutes, then filtered. After removal of the solvent, an oily product was obtained. After addition of 4 ml of methanol, the resulting solution was allowed to stand for some hours at 0° to obtain 0.48 g of crystals of **9b** (55%), mp 185°; ir: 3280, 1675, 1640 cm⁻¹; ¹H-nmr (DMSO-d₆): δ 7.3-8 (m, 21H), 11.3 (s, 1H).

Anal. Calcd. for C₂₇H₂₂N₄O₂ (434.47): C, 74.64; H, 5.10; N, 12.90. Found: C, 74.40; H, 5.11; N, 12.90.

Thermal Decomposition of **9a,b**.

When **9a** was heated for a few minutes at its melting point, it was decomposed into benzaldehyde phenylhydrazone and 5-methyl-3-phenyl-1,3,4-oxadiazol-2(3*H*)-one (**11a**, R = Me), mp 93°, lit [10] mp 92.5-93°. Under the same conditions, **9b** was also decomposed into benzaldehyde phenylhydrazone and the corresponding 3,5-diphenyl-1,3,4-oxadiazol-2(3*H*)-one (**11b**, R = Ph), mp 113°, lit [11] mp 113-114°.

Tetrahydro-1,5-diacetyl-2,4,6-triphenyl-1,2,4,5-tetrazin-3(2*H*)-one (**10**).

A mixture of 165 mg (0.5 mmole) of tetrazinone **6a** and 5 ml of acetic anhydride was refluxed for 3 hours. Excess acetic anhydride was removed by distillation under vacuum and the residue was recrystallized from methanol to yield 149 mg of **10** (72%), mp 155°; ir: 1720, 1660, 1590 cm⁻¹; ¹H-nmr (DMSO-d₆): δ 2.45 (2s,

6H), 7-7.9 (m, 16H).

Anal. Calcd. for C₂₄H₂₂N₄O₃ (414.44): C, 69.55; H, 5.35; N, 13.52. Found: C, 69.51; H, 5.27; N, 13.58.

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