Synthesis of 5-Aryl-3-carbazoyl-1,3,4-oxadiazol-2(3*H*)-one. Derivatives and their Ring Transformation into 5-Benzamido-1,2,4-triazolidine-3,5-dione Derivatives

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Some 5-aryl-3-carbazoyl-1,3,4-oxadiazol-2(3*H*)-one derivatives **6** and **9** have been synthesized in two ways. The expected thermal ring transformation into 2,5-disubstituted 1,3,4-oxadiazoles did not occur but, by acid hydrolysis of 5-aryl-3-[3-benzylidene-2-methyl(or phenyl)carbazoyl]-1,3,4-oxadiazol-2(3*H*)-ones **6**, a new ring transformation took place and the corresponding 4-benzamido-1-methyl(or phenyl)-1,2,4-triazolidine-3,5-dione derivatives **11** were formed. The 4-amino-1-phenyl-1,2,4-triazolidine-3,5-dione (**19**) has been prepared and its structure was confirmed by some reactions.

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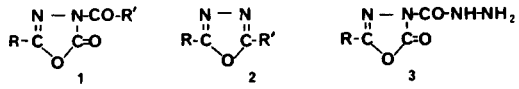
In a previous paper [1], we published the thermal ring transformation of 5-aryl-2-carbazoyl-1,2,3,4-tetrazole derivatives into 5-aryl-2-hydrazino-1,3,4-oxadiazole derivatives which occurred by a nitrogen molecule elimination. The mechanism is analogous to that of the transformation of 2-acyl-5-aryl-1,2,3,4-tetrazoles into 2-alkyl(or aryl)-5-aryl-1,3,4-oxadiazoles studied by Huisgen *et al.* [2]. The ring transformation of 3-acyl-5-aryl-1,3,4-oxadiazol-2(3*H*)-ones **1** into 2-alkyl-5-aryl-1,3,4-oxadiazoles **2** [3] follows the same mechanism with carbon dioxide elimination.

With the aim to study the probable ring transformation of 5-aryl-3-carbazoyl-1,3,4-oxadiazol-2(3*H*)-one derivatives



Scheme 1

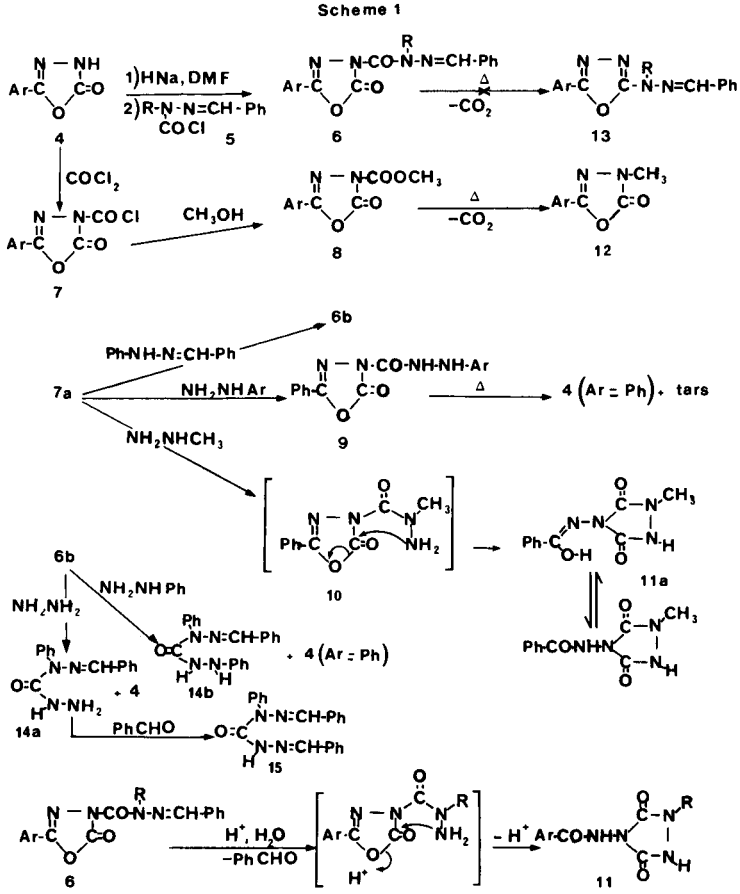
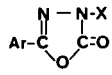


Table I

3-Substituted 5-Aryl-1,3,4-oxadiazol-2(3*H*)-ones



No.	Ar	X	Yield % [a]	Mp °C	Formula	Analyses, % Calcd./Found C	H	N	IR, ν cm^{-1}	^{1}H NMR [b] δ ppm
6a	Ph	CON(Me)N=CHPh	75	171 [c,d]	$C_{17}H_{14}N_4O_3$	63.4 63.4	4.4 4.4	17.4 17.3	1830, 1795, 1720 (b), 1615	3.55 (s, 3H), 7.4-8.1 (m, 10H), 8.25 (s, 1H)
6b	Ph	CON(Ph)N=CHPh	91	154 [e]	$C_{22}H_{16}N_4O_3$	68.7 68.6	4.2 4.2	14.6 14.6	1850, 1805, 1725, 1620	7.2-7.95 (m)
6c	4-Me-Ph	CON(Ph)N=CHPh	95	156 [c]	$C_{23}H_{18}N_4O_3$	69.3 69.4	4.6 4.6	14.1 14.0	1850, 1805, 1720, 1620	2.4 (s, 3H), 7.2-7.8 (m, 15H)
6d	4-MeO-Ph	CON(Ph)N=CHPh	84	158 [f]	$C_{23}H_{18}N_4O_4$	66.7 66.7	4.4 4.4	13.5 13.4	1850, 1800, 1720, 1625	3.8 (s, 3H), 7-8 (m, 15H)
6e	4-Cl-Ph	CON(Ph)N=CHPh	81	162 [f]	$C_{22}H_{15}ClN_4O_3$	63.1 63.2	3.6 3.7	13.4 13.3	1850, 1805, 1725 1620	7.3-8.1 (m)
6f	4-F-Ph	CON(Ph)N=CHPh	75	166 [f]	$C_{22}H_{15}FN_4O_3$	65.7 65.5	3.7 3.8	13.9 14.0	1850, 1805, 1735, 1710, 1625	7.4-8.2 (m)
6g	4-NO_2-Ph	CON(Ph)N=CHPh	55	195 [g]	$C_{22}H_{15}N_5O_5$	61.5 61.3	3.5 3.6	16.3 16.3	1850, 1805, 1730, 1620	7.5-7.85 (m, 11H), 8.25 and 8.55 (2d, 4H)
7a	Ph	COCl	87	111 [h,i]	$C_9H_5ClN_2O_3$	48.1 48.0	2.2 2.2	12.5 12.5	1840 (b), 1770, 1740, 1610	7.1-7.9 (m)
7b	4-Me-Ph	COCl	81	121 [j]	$C_{10}H_7ClN_2O_3$	50.3 50.4	3.0 3.0	11.7 11.6	1845, 1810, 1745 (b), 1625	2.4 (s, 3H), 7.2-7.8 (m, 4H)
8a	Ph	COOMe	98	168 [e,k]						
8b	4-Me-Ph	COOMe	98	164 [e]	$C_{11}H_{10}N_2O_4$	56.4 56.4	4.3 4.3	12.0 11.9	1845, 1805, 1770, 1620	2.4 (s, 3H), 3.95 (s, 3H), 7.45 and 7.8 (2d, 4H)
9a	Ph	CONHNHPh	76	220 [g]	$C_{15}H_{12}N_4O_3$	60.8 60.6	4.1 4.1	18.9 18.8	3410, 3310, 1860, 1820, 1720, 1620	6.7-7.95 (m, 11H), 9.7 (s, 1H)
9b	Ph	CONHNH(4-Me-Ph)	40	177 [c]	$C_{16}H_{14}N_4O_3$	61.9 61.9	4.6 4.5	18.1 18.0	3420, 3310, 1860, 1825, 1770, 1610	2.2 (s, 3H), 6.75 and 7 (2d, 4H), 7.55-8.1 (m, 6H), 9.9 (s, 1H)
9c	Ph	CONHNH(4-NO_2-Ph)	55	275 [l]	$C_{15}H_{11}N_5O_5$	52.8 52.7	3.2 3.2	20.5 20.5	3370, 3310, 1860, 1825, 1710, 1600	7.3-7.9 (m, 6H), 8.3 and 8.6 (2d, 4H), 10 (s, 1H)
12a	Ph	Me	85	102 [e,m]						
12b	4-Me-Ph	Me	80	108 [j,n]	$C_{10}H_{10}N_2O_2$	63.1 63.2	5.3 5.4	14.7 14.7	1780 (b), 1610	2.4 (s, 3H), 3.7 (s, 3H), 7.2-7.8 (m, 4H)

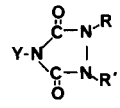
[a] Non optimized yields. [b] All compounds were measured in DMSO-d_6 except **7a**, **7b** and **12b** in deuteriochloroform. [c] Ethanol. [d] Water. [e] Methanol. [f] 1-Propanol. [g] 1-Butanol. [h] Benzene. [i] Cyclohexane. [j] Petroleum ether 40-60. [k] Lit [7] mp 168°. [l] Acetonitrile. [m] Lit [6] mp 101°. [n] Diethyl ether.

3, these compounds have been synthesized by two methods. In the first one, sodium salts of 5-aryl-1,3,4-oxadiazol-2(3*H*)-ones **4** were treated with benzaldehyde 2-chloroformyl-2-methyl(or phenyl)hydrazones **5**, in dry dimethylformamide at 0°, to give 5-aryl-3-[3-benzylidene-2-methyl-(or phenyl)carbazoyl]-1,3,4-oxadiazol-2(3*H*)-ones **6** in good yields (Scheme 1, Table I).

The second method used 5-aryl-3-chloroformyl-1,3,4-oxadiazol-2(3*H*)-ones **7** as the starting material. These new chloroformyl compounds **7** were prepared by a chloroformylation reaction of **4** with phosgene in the presence of pyridine [4,5]. Structure of **7** was confirmed by reaction of **7** with methanol to give known 5-aryl-3-methoxycarbonyl-oxadiazolones **8**, in quantitative yields. Reaction of **7** with

Table II

1,2,4-Triazolidine-3,5-dione Derivatives



No.	Y	R	R'	Yield % [a]	Mp °C	Formula	Analyses, % Calcd./Found C	H	N	IR, ν cm^{-1}	^{1}H NMR [b] δ ppm
11a	PhCONH	Me	H	51	238 [c,d]	$C_{10}H_{10}N_4O_3$	51.3 51.4	4.3 4.3	23.9 23.7	3170 (b), 1770, 1720, 1705, 1665, 1600	3.15 (s, 3H), 7.4-8.15 (m, 5H), 11 (bs, 1H), 11.2 (s, 1H)
11b	PhCONH	Ph	H	72	240 [c,d]	$C_{15}H_{12}N_4O_3$	60.8 60.7	4.1 4.1	18.9 19.0	3180 (b), 1805, 1790, 1720, 1655, 1590	7.1-8 (m, 10H), 11.25 (s, 1H), 11.5 (b, 1H)
11c	4-Me-PhCONH	Ph	H	65	228 [c,d]	$C_{16}H_{14}N_4O_3$	61.9 61.8	4.6 4.6	18.1 18.1	3200 (b), 1800, 1735, 1720, 1660, 1610, 1595	2.35 (s, 3H), 7-7.8 (m, 9H), 11.15 (s, 1H), 11.5 (b, 1H)
11d	4-Cl-PhCONH	Ph	H	65	275 [c,d]	$C_{15}H_{11}ClN_4O_3$	54.5 54.5	3.4 3.4	16.9 16.8	3200 (b), 1800, 1730, 1700, 1660, 1600	7.1-8 (m, 9H), 11.4 (s, 1H), 11.5 (b, 1H)
11e	4-F-PhCONH	Ph	H	95	248 [c,d]	$C_{15}H_{11}FN_4O_3$	57.3 57.2	3.5 3.5	17.8 17.9	3320, 3080 (b), 1800, 1770, 1690, 1655, 1600	7.3-8.3 (m, 9H), 11.5 (b, 1H), 11.6 (s, 1H)
11f	4-NO_2-PhCONH	Ph	H	75	305 dec [c]	$C_{15}H_{11}N_5O_5$	52.8 52.9	3.3 3.3	20.5 20.4	3330, 3100 (b), 1775, 1770, 1685, 1650, 1600	7.2-7.9 (m, 5H), 8.35 and 8.6 (2d, 4H), 11.5 (b, 1H), 11.95 (s, 1H)
16	PhCONH	Ph	COMe	75	188 [c]	$C_{17}H_{14}N_4O_4$	60.4 60.3	4.2 4.2	16.6 16.6	3240 (b), 1815, 1765, 1740, 1665, 1600	2.5 (s, 3H), 7.2-8.05 (m, 10H), 11.7 (s, 1H)
17	PhCO(MeCO)N	Ph	COMe	70	165 [c]	$C_{19}H_{16}N_4O_5$	60.0 59.8	4.2 4.2	14.7 14.8	1815, 1765, 1740, 1720, 1695, 1600	2.55 (s, 6H), 7.25-7.85 (m, 10H)
19	NH_2	Ph	H	78	248 [c]	$C_8H_8N_4O_2$	50.0 50.1	4.2 4.2	29.2 29.1	3340, 3220, 3080 (b), 1750, 1700, 1685 1600	4.8 (bs, 2H), 7-7.8 (m, 5H), 11 (bs, 1H)
20	PhCH=N	Ph	H	95	174 [e]	$C_{15}H_{12}N_4O_2$	64.3 64.3	4.3 4.4	20.0 20.1	3160 (b), 1780, 1700, 1680, 1600	7.1-8 (m, 11H), 11.5 (b, 1H)
22	NH_2	Ph	CH_2Ph	61	166 [c,d]	$C_{15}H_{14}N_4O_2$	63.8 63.7	5.0 5.0	19.8 19.9	3330, 3275, 1770, 1690 (b), 1590 (b)	4.6 (s, 2H), 5.05 (s, 2H), 6.95-7.65 (m, 10H)

[a] Non optimized yields. [b] All compounds were measured in DMSO-d_6. [c] Ethanol. [d] Water. [e] 1-Butanol.

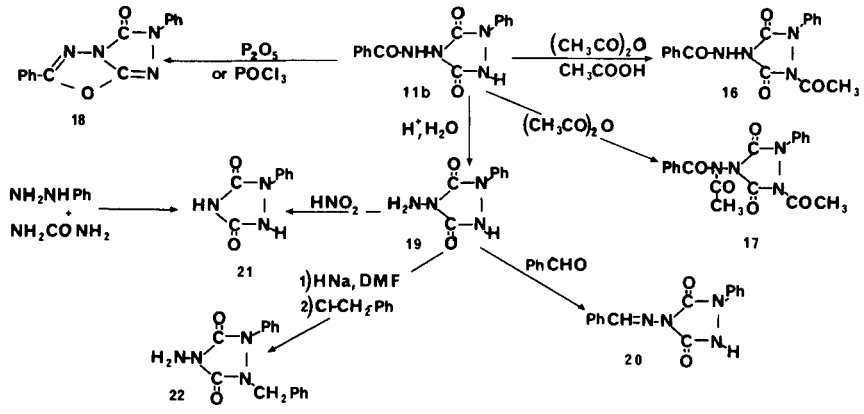
amines and rearrangement study of the resulting products will be published later. Compound **7a** did not react easily with benzaldehyde phenylhydrazone to give **6b**. The yield was very low.

Treatment of **7a** with arylhydrazines gave 3-(3-aryl-carbazoyl)-5-phenyl-1,3,4-oxadiazol-2(3*H*)-ones **9** but, with methylhydrazine, the expected analogue **9** was not obtained because **7a** reacted only at N-1 of methylhydrazine to give the unstable intermediate **10**. This one was converted into 4-benzamido-1-methyl-1,2,4-triazolidine-3,5-dione (**11a**) *via* an amino group intramolecular attack at the heterocyclic carbonyl group with ring opening, then cyclization.

As already described, thermal ring transformations of **8** gave 5-aryl-3-methyl-1,3,4-oxadiazol-2(3*H*)-ones **12** [6] by a radical mechanism [7]. On the other hand, at temperatures equal or above 250°, 3-carbazoyl derivatives **6** failed to give the expected ring transformation in compounds **13** but were decomposed into tarry products. On heating 3-carbazoyl compounds **9** at 250°, only the 5-phenyloxadiazolone **4** (Ar = Ph) was obtained besides tarry products.

Acid hydrolysis of oxadiazolones **6** gave intermediates **10** which cyclized instantaneously in very good yields into 4-benzamido-1-methyl(or phenyl)-1,2,4-triazolidine-3,5-dione derivatives **11** (Table II) by a mechanism similar to that of the reaction between **7a** and methylhydrazine. Compounds **11** were prepared for industrial purposes.

Scheme 2



Compound **11b** was also obtained by reaction of 2,4-dinitrophenylhydrazine with **6b**. Treatment of **6b** with hydrazine hydrate or phenylhydrazine gave a mixture of 5-phenyloxadiazolone **4** (Ar = Ph) and 1-benzylidene-2-phenylcarbonohydrazide derivatives **14** [8,9]. By reaction of benzaldehyde with **14a**, the dibenzylidene derivative **15** was formed.

Triazolidinedione **11b** was monoacetylated with acetic anhydride in acetic acid and diacetylated in acetic anhydride alone to give **16** and **17**, respectively (Scheme 2). An attempted cyclization of **11b** into **18** by phosphorus anhydride was unsuccessful.

A long acid hydrolysis (5 hours) of compound **11b** resulted in removal of the benzamido group with formation of the new 4-amino-1-phenyl-1,2,4-triazolidine-3,5-dione (**19**). Under the same conditions, **11a** was decomposed and the methyl analogue of **19** was not obtained.

The structure of the first synthesized mono-1-aryl-substituted 4-amino-1,2,4-triazolidine-3,5-dione **19** was confirmed by three reactions and physico-chemical data. Reaction of **19** with benzaldehyde gave the benzylidene derivative **20**. Nitrous deamination of **19** gave 1-phenyl-1,2,4-triazolidine-3,5-dione (**21**) which was identical with the compound prepared from phenylhydrazine and urea when the temperature was slowly raised to 150-160° [10,11]. Treatment of the sodium salt of **19** (prepared from sodium hydride in anhydrous dimethylformamide) with benzyl chloride afforded 4-amino-2-benzyl-1-phenyl-1,2,4-triazolidine-3,5-dione (**22**).

Physico-chemical data of all new produts are compiled in Tables I and II.

The ir spectra of oxadiazolone derivatives **6**, **7**, **8** and **9** showed three bands (1860-1830, 1825-1770 and 1770-1710 cm^{-1}) assignable to cyclic and exocyclic carbonyl groups. This excess of absorption bands could be the result of possible rotational isomerism and a Fermi resonance effect, as proposed previously for some 3-alkoxycarbonyloxadiazolones [7b]. The excess of carbonyl absorption bands of 4-amino-1,2,4-triazole-3,5-dione derivatives **11**, **19** and **20** could be due to numerous cyclic tautomeric forms in agreement with the explication given for carbonyl absorption bands of the 4-methyl-1-phenyl-1,2,4-triazole-3,5-dione ir spectrum. This compound can exist in three tautomeric forms [12]. Other compounds **16**, **17** and **22** showed normal ir carbonyl absorption bands because they presented no cyclic tautomeric forms.

EXPERIMENTAL

Melting points (uncorrected) were determined with a Buchi oil heated apparatus except for **11f** which was observed with a Maquenne apparatus. The ir spectra were recorded on a Perkin Elmer 1310 spectrophotometer as potassium bromide disks. The ^{1}H-nmr spectra were obtained in DMSO-d_6 or deuteriochloroform on a Brucker WP 80 spectrometer and are reported as δ values (ppm) relative to tetramethylsilane as an internal standard.

Benzaldehyde 2-Chloroformylhydrazones **5**.

Compound **5b** (R = Ph) was synthesized as previously described [9,13] but the preparation of **5a** (R = Me) [14] was modified.

A solution of 13.4 g (0.1 mole) of benzaldehyde methylhydrazone and 8 g (0.1 mole) of dry pyridine in 30 ml of dry benzene was added slowly with vigorous stirring to a solution of 15 g (0.15 mole) of phosgene in 175 ml of dry benzene. The mixture was stirred for 30 minutes at 25° and for 30 minutes at 70-80° on a water bath, then filtered. The collected pyridine hydrochloride was washed with 50 ml of dry benzene. After removal of the solvents, the red oily residue was solubilized in a minimum amount of boiling cyclohexane. Carbon black was added and the hot solution was filtered. On cooling, compound **5a** crystallized giving 14.7 g (75%), mp 88°; lit [14] mp 88°.

5-Aryl-3-[benzylidene-2-methyl(or phenyl)carbazoyl]-1,3,4-oxadiazol-2(3*H*)-ones **6**.

A solution of 10 mmoles of 5-aryloxadiazolone **4** in 40 ml of dry dimethylformamide was added slowly to a cold suspension of 0.40 g (10 mmoles) of sodium hydride (60% in oil) in 40 ml of dry dimethylformamide. After addition and heating for 30 minutes on a water bath at 50-60°, hydrogen gas evolution ceased. After cooling at 0°, a solution of 10 mmoles of **5** in 20 ml of dry ethyl acetate was added dropwise under stirring. After heating on a water bath at 70-80° for 30 minutes, ethyl acetate and 30 ml of dimethylformamide were evaporated *in vacuo*. The resulting solution was poured into 300 ml of cold water. The precipitate

was filtered and recrystallized.

5-Aryl-3-chloroformyl-1,3,4-oxadiazol-2(3*H*)-ones **7**.

A solution of 20 mmoles of **4** in 300 ml of dry ethyl acetate and 16 g of dry pyridine was added to a vigorously stirred solution of 3 g (30 mmoles) of phosgene in 200 ml of dry toluene at 0°. After addition, the temperature was raised slowly to 70-80° in 30 minutes and maintained for 30 minutes. The filtered pyridine hydrochloride was washed with 50 ml of dry benzene and the filtrate was evaporated *in vacuo*. The resulting white solid **7** was recrystallized. These very reactive compounds were kept in a dessicator.

5-Aryl-3-methoxycarbonyl-1,3,4-oxadiazol-2(3*H*)-ones **8**.

These compounds **8** were formed instantaneously in quantitative yields by addition of methanol to chloroformyl compounds **7**.

3-(3-Arylcarbazoyl)-5-phenyl-1,3,4-oxadiazol-2(3*H*)-ones **9**.

A solution of 2.24 g (10 mmoles) of **7a** and 10 mmoles of arylhydrazine in 60 ml of dry benzene was refluxed for 20 minutes. After removal of the solvent, compounds **9** were recrystallized. With 4-nitrophenylhydrazine, the reaction was effected in ethyl acetate with addition of a stoechiometric quantity of dry pyridine.

Reaction of **7a** with Methylhydrazine. Formation of 4-Benzamido-1-methyl-1,2,4-triazolidine-3,5-dione (**11a**).

A solution of 2.24 g (10 mmoles) of **7a** in 30 ml of ethyl acetate was slowly added to a stirred solution of 0.92 g (20 mmoles) of methylhydrazine in 40 ml of ethyl acetate. The mixture was stirred for 1 hour. After removal of the solvent, the resulting residue **11a** was washed with water and recrystallized.

5-Aryl-3-methyl-1,3,4-oxadiazol-2(3*H*)-ones **12**.

Compounds **8** were heated at dryness at 200° until carbon dioxide evolution ceased. The resulting compounds **12** were recrystallized.

Thermolysis of **9**.

On heating **9a** and **9d** at dryness at 250° until carbon dioxide evolution ceased, the same compound **4** (Ar = Ph) was obtained besides tarry products and separated by column chromatography on silica gel 60 0.05-0.2 mm (Macherey-Nagel) using ethyl acetate:petroleum ether 40-60 (1:1) as the eluent.

Acid Hydrolysis of **6**. Preparation of 4-Benzamido-1-methyl(or phenyl)-1,2,4-triazolidine-3,5-diones **11**.

A solution of 1 mmole of **6** in 60 ml of ethanol, 5 ml of water and 0.5 ml of concentrated hydrochloric acid was refluxed for 45 minutes. After removal of the solvents, the resulting powder was washed with diethyl ether and recrystallized.

Hydrazinolysis of **6b**.

A solution of 1.9 g (5 mmoles) of **6b** and 5 mmoles of methyl or phenylhydrazine in 30 ml of 1-propanol was refluxed for 1 hour. After removal of the solvent, an oily product was obtained. After addition of 100 ml of diethyl ether, compounds **14** precipitated and were filtered. Oxadiazolone **4** (Ar = Ph) was obtained after evaporation of the ethereal filtrate.

1-Benzylidene-2-phenylcarbonohydrazide (**14a**).

This compound was recrystallized from ethyl acetate giving 0.65 g (51%), mp 202°; ir: 3320, 1670, 1620, 1600 cm^{-1}; nmr (DMSO-d_6): δ 4.05 (s, 2H), 7-7.75 (m, 11H), 8.5 (s, 1H).

Anal. Calcd. for $C_{14}H_{14}N_4O$: C, 66.1; H, 5.6; N, 22. Found: C, 66.3; H, 5.5; N, 22.1.

1-Benzylidene-2,5-diphenylcarbonohydrazide (**14b**).

This compound was recrystallized from 1-propanol giving 0.86 g (52%), mp 178° [8]; ir: 3420, 3300, 1675, 1595 cm^{-1}; nmr (DMSO-d_6): δ 6.5-7.9 (m, 17H), 9.4 (s, 1H).

Anal. Calcd. for $C_{20}H_{18}N_4O$: C, 72.7; H, 5.5; N, 17. Found: C, 72.7; H, 5.5; N, 17.

Under the same conditions as above and in the presence of 2,4-dinitrophenylhydrazine, **6b** gave **11b** besides benzaldehyde 2,4-dinitrophenylhydrazone.

Benzaldehyde 2-Phenylcarbonodihdyrazone (**15**).

A solution of 0.5 g (2 mmoles) of **14a** and 0.26 g (2.5 mmoles) of benzaldehyde in 20 ml of ethanol was refluxed for 10 minutes. After removal of the solvent, the residue **15** was recrystallized from ethyl acetate giving 0.65 g (95%), mp 192°; ir: 3340, 1705 (broad), 1600 cm^{-1}; nmr (DMSO-d_6): δ 7.15-8 (m, 17H), 8.6 (s, 1H).

Anal. Calcd. for $C_{21}H_{18}N_4O$: C, 73.7; H, 5.3; N, 16.4. Found: C, 73.7; H, 5.4; N, 16.5.

2-Acetyl-4-benzamido-1-phenyl-1,2,4-triazolidine-3,5-dione (**16**).

A solution of 0.296 g (1 mmole) of **11b** in 10 ml of acetic acid and 0.5 ml of acetic anhydride was refluxed for 1 hour. After removal of the solvents, the solid **16** was recrystallized.

2-Acetyl-4-(*N*-acetylbenzamido)-1-phenyl-1,2,4-triazolidine-3,5-dione (**17**).

A solution of 0.296 g (1 mmole) of **11b** in 10 ml of acetic anhydride was refluxed for 20 minutes. After removal of the solvents, an oily product was obtained which slowly crystallized, and the solid was recrystallized.

4-Amino-1-phenyl-1,2,4-triazolidine-3,5-dione (**19**).

A suspension of 11.85 g (40 mmoles) of **11b** in 300 ml of 3 *N* hydrochloric acid and 100 ml of ethanol was refluxed for 5 hours. On cooling, **19** crystallized, was filtered and recrystallized.

4-Benzylidenamino-1-phenyl-1,2,4-triazolidine-3,5-dione (**20**).

A solution of 0.38 g (2 mmoles) of **19** and 0.25 g (2.5 mmoles) of benzaldehyde in 20 ml of 1-butanol was refluxed for 30 minutes. After removal of the solvent, the residue **20** was recrystallized.

Nitrous Deamination of **19**.

A solution of 0.5 g (7 mmoles) of sodium nitrite in 3 ml of water was added dropwise at 0-5° to a solution of 0.96 g (5 mmoles) of **19** in 30 ml of acetic acid and 0.3 ml of concentrated hydrochloric acid. The mixture was stirred for 30 minutes at the same temperature and poured into 100 ml of cold water. The precipitate **21** appeared slowly. It was filtered and recrystallized from ethyl acetate giving 0.59 g (67%), mp 264°; lit [10] mp 268°.

Alkylation of **19** into 4-Amino-2-benzyl-1-phenyl-1,2,4-triazolidine-3,5-dione (**22**).

To a solution of 0.96 g (5 mmoles) of **19** in 20 ml of dry dimethylformamide, 0.2 g (5 mmoles) of sodium hydride (60% in oil) was added. When hydrogen gas evolution ceased, the mixture was heated at 60-80° for 10 minutes. After cooling at 0°, a solution of 0.63 g (5 mmoles) of benzyl chloride in 5 ml of dry dimethylformamide was added slowly. After heating at 60-80° for 30 minutes, the mixture was poured into 150 ml of cold water. Compound **22** precipitated, was filtered and recrystallized.

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[4] A sole example of compound **7** has been used in the literature [5], namely 4-chloroformyl-2-methyl-1,3,4-oxadiazolidine-5-one but it was not described.

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[8] The reaction of phenylhydrazine with chloroformylhydrazone **5b** in ethanol at room temperature was reported to give the expected compound **14b** [8]. However, a new experiment under the same conditions showed us the simultaneous formation of two isomers: the acyclic one **14b** which was minor and a cyclic one, the tetrahydro-2,4,6-triphenyl-1,2,4,5-tetrazin-5-one (**18**). This result will be published later.

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[11] In this reaction without solvent, compounds **21** and 4-anilino-1,2,4-triazolidine-3,5-dione were formed. If refluxing anhydrous dimethylformamide was the solvent, only **21** was obtained.

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