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Four 3-(3-benzylidene-2-phenylcarbazoyl)-2(3*H*)-benzoxazolone derivatives **3** have been synthesized from benzoxazolone derivatives **1** and benzaldehyde *N*-chloroformylphenylhydrazone **2**. By acid hydrolysis, these compounds yielded 3-(2-phenylcarbazoyl)-2(3*H*)-benzoxazolone derivatives **4** which were not isolated and were transformed *via* an intramolecular reaction into 4-(2-hydroxyphenyl)-1-phenyl-1,2,4-triazolidine-3,5-dione derivatives **5** in a good yield. Attempts to cyclize these compounds by intramolecular elimination of water into tricyclic compounds **6** with various dehydrating agents were unsuccessful.

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In our previous papers [1,2] we reported the thermal ring transformation of 5-aryl-2-carbazoyl-1,2,3,4-tetrazole derivatives **A** into 5-aryl-2-hydrazino-1,3,4-oxadiazoles **B** and the transformation of 5-aryl-3-carbazoyl-1,3,4-oxadiazol-2(3*H*)-one derivatives **C** into 4-benzamido-1,2,4-triazolidine-3,5-diones **D** (Scheme 1).

Similarly, this paper describes the new ring transformation of 3-(2-phenylcarbazoyl)-2(3*H*)-benzoxazolone derivatives **3** into 4-(2-hydroxyphenyl)-1-phenyl-1,2,4-triazolidine-3,5-diones **5**.

Some cyclic transformations of 2(3*H*)-benzoxazolone derivatives into triazinones [3], *N*-(2-hydroxyphenyl)-2-oxazolidinones [4] and 2-imidazolidinones [5] are known.

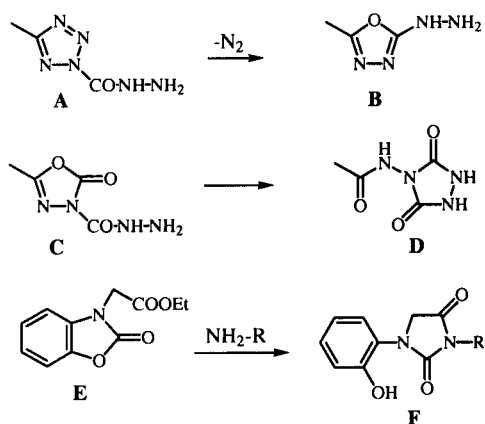
The 2(3*H*)-benzoxazolones **1a-d** were prepared according to a classical method [6] by a reaction of *o*-aminophenols with urea (Scheme 2). The respective 3-(3-benzylidene-2-phenylcarbazoyl) derivatives, **3a-d**, were obtained by the reaction of benzaldehyde *N*-chloroformyl-*N*-phenylhydrazone **2** with the sodium salts of **1a-d**. Compound **2** was formed by reaction of phosgene with

Table 1
Physicochemical Data of Compounds **3** and **5**

Compound	R	Yield % [a]	Mp °C	Formula (mol.wt.)	Analysis, %			UV [b] λ_{\max} nm (log ϵ)	IR ν cm ⁻¹	¹ H NMR [c] δ ppm
					Calcd.	Found				
					C	H	N			
3a	H	64	124 [d]	C ₂₁ H ₁₅ N ₃ O ₃ (357.35)	70.57 70.65	4.23 4.27	11.75 11.61	276 (4.75)	1790, 1690	7-7.8 (m, 14H ar. + 1H, -CH=N-)
3b	CH ₃	68	142 [d]	C ₂₂ H ₁₇ N ₃ O ₃ (371.37)	71.14 71.30	4.61 4.68	11.31 11.20	280 (4.39)	1794, 1710	2.35 (s, 3H, CH ₃), 7-7.8 (m, 13 H ar. + 1H, -CH=N-)
3c	Cl	71	171 [d]	C ₂₁ H ₁₄ ClN ₃ O ₃ (391.79)	64.37 64.42	3.60 3.70	10.72 10.55	282 (4.43)	1795, 1695	6.7-8 (m, 13H ar. + 1H, -CH=N-)
3d	NO ₂	77	150 [e,f]	C ₂₁ H ₁₄ N ₄ O ₅ (402.35)	62.68 62.82	3.50 3.50	13.92 13.72	282 (4.51)	1800, 1685	7.1-7.9 (m, 10 H ar. + 1H, -CH=N-) 8.2 (d, 1H ar.), 8.4 (d, 1H ar.), 8.4 (s, 1H ar.)
5a	H	73	212 [g,f]	C ₁₄ H ₁₁ N ₃ O ₃ (269.24)	62.44 62.47	4.11 4.25	15.60 15.45	242 (4.34) 280 (4.30)	3350, 3290 1750, 1660	7.65-6.87 (m, 9H ar.), 10 (br s, 1H, OH), 11.33 (s, 1H, NH)
5b	CH ₃	78	202 [e]	C ₁₅ H ₁₃ N ₃ O ₃ (283.27)	63.59 63.64	4.62 4.71	14.83 14.77	242 (4.25) 286 (4.23)	3360, 3340 1750, 1660	2.23 (s, 3H, CH ₃), (m, 8H ar.) 7.64-6.869.76 (s, 1H, OH), 1130 (s, 1H, NH)
5c	Cl	81	230 [h,i]	C ₁₄ H ₁₀ ClN ₃ O ₃ (303.69)	55.36 55.50	3.31 3.33	13.83 13.79	238 (sh) 288 (4.23)	3340, 3260 1755, 1675	6.98-7.63 (m, 8H ar.), 10.37 (s, 1H, OH) 11.38 (s, 1H, NH)
5d	NO ₂	61	> 300 [d]	C ₁₄ H ₁₀ N ₄ O ₅ (314.24)	53.50 53.62	3.20 3.20	17.82 17.68	260 (4.26) 274 (sh), 306 (sh)	3175 (broad) 1750, 1680	7.16-7.64 (m, 6H ar.), 8.23-8.44 (m, 2H ar.) 11.3-12.1 (br s, 2H, OH, NH)

[a] Non optimized yields. [b] Compound **5d** was measured in MeOH and the other compounds were measured in CH₃CN. [c] Compounds **3** were measured in CDCl₃, and compounds **5** were measured in DMSO d₆. [d] 1-Butanol. [e] Ethyl acetate. [f] Petroleum ether 40-60. [g] Diethyl ether. [h] Ethanol. [i] Water.

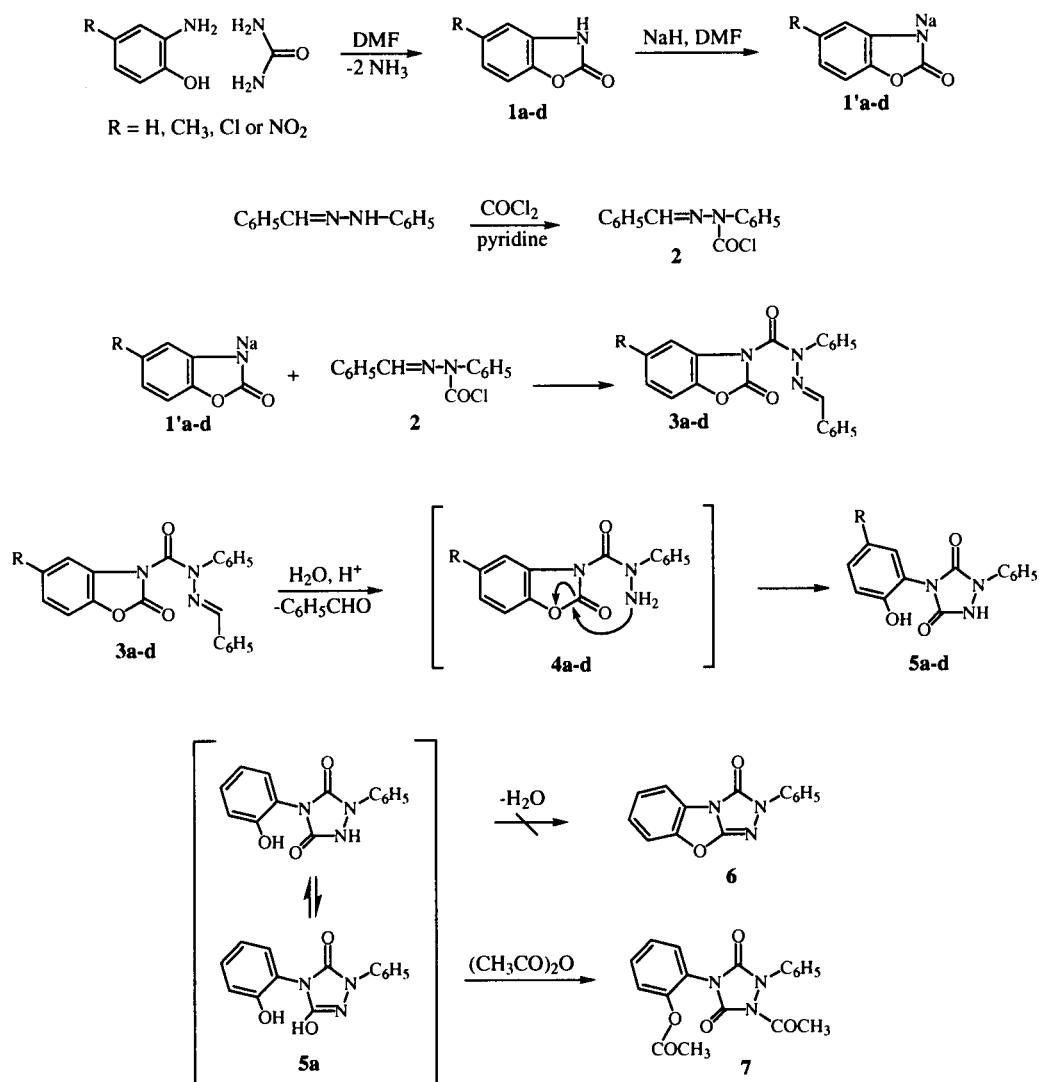
Scheme 1



benzaldehyde phenylhydrazone in anhydrous ethyl acetate, in the presence of pyridine. Sodium salts of **1a-d** resulted from the treatment of the corresponding heterocycles with sodium hydride in anhydrous dimethylformamide.

Acid hydrolysis of compounds **3a-d** gave the unstable (not isolated) free carbazoyl derivatives **4a-d** which cyclized instantaneously into 4-(2-hydroxyphenyl)-1-phenyl-1,2,4-triazolidine-3,5-dione derivatives **5a-d**, in good yields. The transformation involved NH_2 nucleophilic intramolecular attack of the cyclic oxo group with ring opening of the oxazolone and ring closure into triazolidinedione. This cyclic transformation is analogous to that reported by us in the reaction between ethyl 2-oxo-3(2*H*)-benzoxazoleacetate derivatives **E** and primary amines [7] yielding 1-(2-hydroxyphenyl)-2,4-imidazolidinedione derivatives **F** (Scheme 1).

Scheme 2



Physicochemical data for all new products **3** and **5** are given in Table 1. Assignments for the structures of the new products were based on elemental analyses, ir and ^1H nmr spectra.

Attempts to form a tricyclic molecule **6** by intramolecular elimination of water from **5a** using various dehydrating agents were unsuccessful. With acetic anhydride, **5a** gave the diacetyl derivative **7**.

EXPERIMENTAL

Melting points were determined on a Büchi 510 oil heated apparatus and are uncorrected. The uv spectra were measured with a Hewlett-Packard HP 8452 spectrophotometer. The ir spectra were recorded on a Perkin-Elmer 1310 spectrometer in potassium bromide disks. The ^1H nmr spectra were obtained in DMSO- d_6 or deuteriochloroform on a Bruker AC 200 spectrometer and are reported as δ values (ppm) relative to tetramethylsilane as an internal standard.

2(3H)-benzoxazolones (**1a-d**).

These compounds were prepared according to a classical method [6].

Benzaldehyde *N*-chloroformyl-*N*-phenylhydrazone (**2**).

This compound was synthesized according to a previously described method [8].

3-(3-Benzylidene-2-phenylcarbazoyl)-2(3H)-benzoxazolone derivatives (**3a-d**).

A solution of benzoxazolone **1** (10 mmol) in 15 ml of dry dimethylformamide was slowly added to a cold suspension of 0.24 g (10 mmol) of sodium hydride in 10 ml of dry dimethylformamide. After addition and heating for 15 minutes on a water bath at 30-40°, hydrogen gas evolution ceased. After cooling at 5°, a solution of 2.7 g (10 mmol) of **2** in 15 ml of dry dimethylformamide was added dropwise under strong stirring. After heating on a water bath for 30 minutes at 40-50°, and then cooling at 10°, the solvent was evaporated under reduced pressure. The resulting material was dissolved in 1-butanol. The solution was filtered and the solvent evaporated. The resulting product **3** was recrystallized from an adequate solvent [9] (Table 1).

4-(2-Hydroxyphenyl)-1-phenyl-1,2,4-triazolidine-3,5-diones (**5a-c**).

A solution of **3a**, **b** or **c** (15 mmol) in 50 ml of ethanol and 1 ml of 10% commercial hydrochloric acid was refluxed for 25 minutes (**3a**), 75 minutes (**3b**), or 45 minutes (**3c**), respectively. After evaporation of the solvent and excess of hydrochloric acid at half

volume, the solution was poured into 50 ml of ice-water. The mixture was extracted twice with 25 ml of diethyl ether. The ether solution was washed twice with 10 ml of water, dried over dry magnesium sulfate, filtered, and the filtrate evaporated. The resulting crop was recrystallized with difficulty from an adequate solvent (Table 1).

4-(2-Hydroxy-5-nitrophenyl)-1-phenyl-1,2,4-triazolidine-3,5-dione (**5d**).

A solution of **3d** (5 mmol) in 20 ml of ethanol and 3 ml of 10% commercial hydrochloric acid was refluxed for 20 minutes. After cooling, the mixture was poured into 100 ml of ice-water. Compound **5d** precipitated slowly. It was filtered, washed with 10 ml of water, dried, and then recrystallized from an adequate solvent (Table 1).

1-Acetyl-4-(2-acetyloxyphenyl)-2-phenyl-1,2,4-triazolidine-3,5-dione (**7**).

To 20 ml of acetic anhydride was added 2.7g (10 mmol) of **5a**. The mixture was refluxed for one hour. Excess of acetic anhydride was evaporated under reduced pressure, and the resulting solid was recrystallized from ethanol to give 2.9 g of **7** (yield: 83%), mp 153°; ir: ν 1730 (broad) 1790 (C=O) cm^{-1} ; ^1H nmr (deuteriochloroform): δ ppm 7.6-7.1 (m, 9H ar), 2.6 (s, 3H), 2.1 (s, 3H).

Anal. Calcd. for $\text{C}_{18}\text{H}_{15}\text{N}_3\text{O}_5$: C, 61.18; H, 4.27; N, 11.89. Found: C, 61.31; H, 4.20; N, 11.90.

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- [9] Recrystallizations of compounds **3** were difficult. A very slow cooling of the hot saturated alcoholic solution followed by standing at 4-5° for one day were necessary to obtain crystals. Otherwise, an oil was formed which crystallized with difficulty after a few days.