

Vladimir L. Rusinov [a], Grigori V. Zyryanov [a], Tatjana L. Pilicheva [a],
Oleg N. Chupakhin [a], Hans Neunhoeffer [b]

[a] Urals State Technical University, Ekaterinburg, 620002, Russia

[b] Institut für Organische Chemie, Technische Hochschule, Petersenstr. 22, D-64287 Darmstadt, Germany

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3-Aryl-1,2,4-triazin-5(2H)-ones **1a-c** react with indoles **2a-c** in trifluoroacetic acid/chloroform or in boiling butanol or acetic acid to give 3-aryl-6-(indolyl-3)-1,6-dihydro-1,2,4-triazin-5(2H)-ones **3a-g**. Oxidation of the dihydro-1,2,4-triazin-5(2H)-ones **3a-e** afforded 6-(indolyl-3)-1,2,4-triazin-5(2H)-ones **4a-e**, products of nucleophilic substitution of hydrogen in **1a-c**. Refluxing **1b** with *N*-methylpyrrole **5b** in butanol for an extended time resulted in the formation of 3-(4-chlorophenyl)-6-(1-methylpyrrolyl-2)-1,2,4-triazin-5(2H)-one **4h**. The reaction of **1a-c** with indoles **2a-c**, pyrroles **5a,b**, 1,3-dimethyl-2-phenylpyrazol-4-one (**8**) and aminothiazoles **9a,b** in acetic anhydride affords the 1-acetyl-3-aryl-6-hetaryl-1,6-dihydro-1,2,4-triazin-5(2H)-ones **6a-s**. Reaction of **1a-c** with *N*-methylpyrrole **5b** in acetic anhydride gives beside the 1:1 addition products **6h-k** also the 2:1 addition products **7a-c**.

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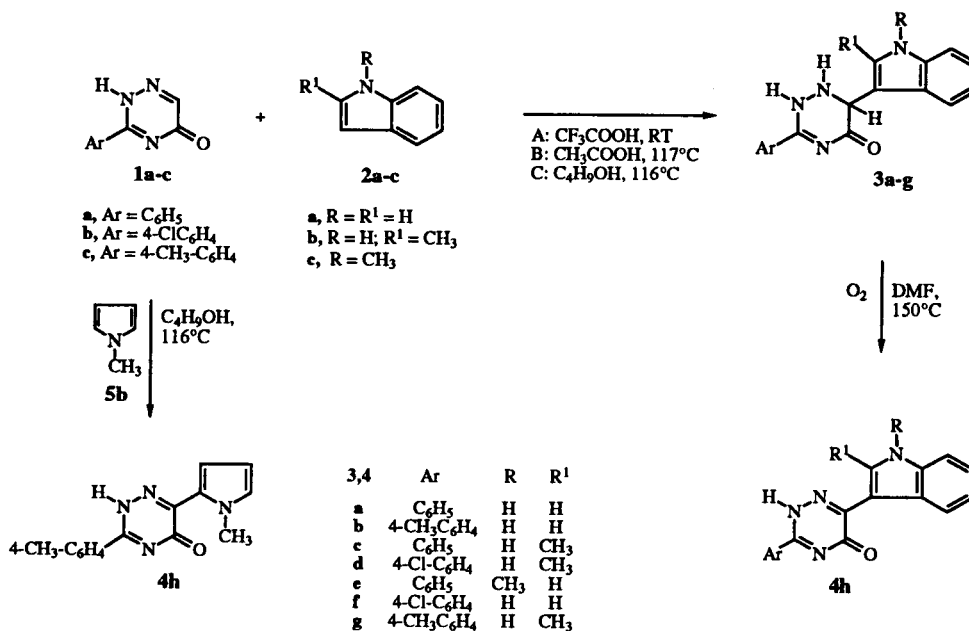
Nucleophilic substitution of hydrogen in heteroarenes is a widely used method for the introduction of various carbon-nucleophiles into six-membered heterocycles containing one or two nitrogen atoms [1]. However, interaction of 1,2,4-triazines with carbon-nucleophiles is reported only in a few cases. Addition of Grignard reagents starts at the 5-position, if this position is substituted, the nucleophile adds to the 6-position and finally to the 3-position. Starting from the parent 1,2,4-triazine, 3,5,6-triaryl-1,2,4-triazines were prepared by subsequent addition of Grignard reagents to the 1,2,4-triazine and oxidation of the formed dihydro-1,2,4-triazines [2,5].

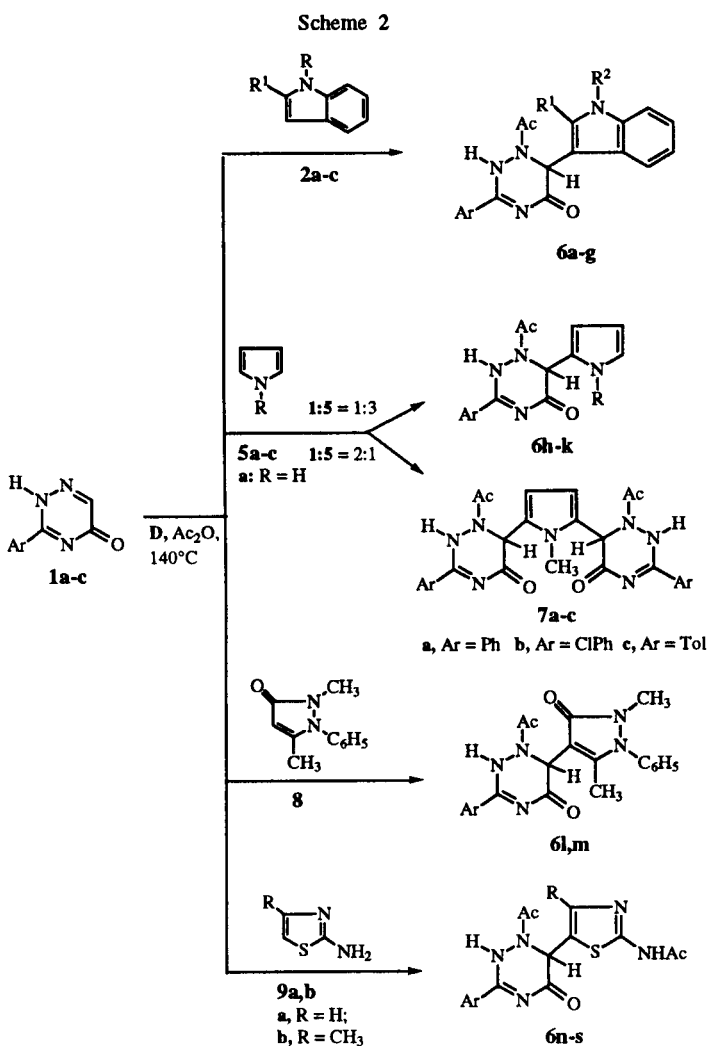
Oxidation of the adducts obtained from 3-phenyl-6-methyl-1,2,4-triazine and cyanoacetate, benzyl cyanide or

acetophenone afforded the corresponding 5-substituted 1,2,4-triazines [4]. Carbanions containing leaving groups at the carbanionic center react with 1,2,4-triazines according to the vicarious nucleophilic substitution scheme replacing hydrogen atoms in the 5-, 3- and 6-positions with the carbanionic moiety. The reactivity of the various positions decreases in the order 5, 3, 6 [6-10]. This reactivity differs from that toward Grignard reagents. 3,4,6-Trimethyl-2,3-dihydro-1,2,4-triazin-5(4H)-one or 4,6,6-trimethyl-1,6-dihydro-1,2,4-triazin-5(4H)-one was obtained, when 4,6-dimethyl-1,2,4-triazin-5(4H)-one was allowed to react with methyl iodide [11].

In the present work a simple method for the introduction of electron-rich aromatic and CH-active heterocycles into 1,2,4-triazin-5(2H)-ones is reported. The method described

Scheme 1





	6	a	b	c	d	e	f	g	h	i	j	k	n	o	p	q	r	s
Ar	Ph	ClPh	Tol	Ph	Tol	Ph	Tol	Ph	Tol	Ph	Tol	Ph	ClPh	Tol	Ph	ClPh	Tol	Ph
R	H	H	H	Me	Me	H	H	H	H	H	Me	Me	H	H	H	Ph	Ph	Ph
R ¹	H	H	H	H	H	H	Me	Me										

Ph = C₆H₅; Tol = 4-CH₃-C₆H₄; Cl-C₆H₄

is the simplest way preparing these compounds which show interesting biological activities.

We have found that 1,2,4-triazin-5(2*H*)-ones **1a-c**, activated by protonation, react with indole (**2a**) and its derivatives **2b,c** smoothly at room temperature in a mixture of trifluoroacetic acid/chloroform (method A) or in boiling acetic acid (method B) to give the 3-aryl-6-(indolyl-3)-1,6-dihydro-1,2,4-triazin-5(2*H*)ones **3a-g** (Scheme 1) in good yields.

Without acidic catalysis the 1,2,4-triazin-5(2*H*)-ones **1a-c** are less susceptible for a nucleophilic attack, and indeed the reaction of **1a-c** with indoles **2a-c** in boiling butanol (method C) proceeds very slowly. Compounds **3** can be regarded as intermediates in the nucleophilic substitution of hydrogen in 1,2,4-triazin-5(2*H*)-ones **1a-c**. Aromatization of the adducts **3** - spontaneously by bubbling air through the solutions in DMF - affords the corresponding 3-aryl-6-hetaryl-1,2,4-triazin-5(2*H*)-ones **4a-e**.

In a similar way, but without isolation of the intermediate dihydro-1,2,4-triazin-5(2*H*) one, 3-(4-tolyl)-6-(1-methylpyrrol-2-yl)-1,2,4-triazin-5(2*H*)-one (**4h**) was obtained from the reaction of **1b** with 1-methylpyrrole (**5b**) in boiling butanol.

Further studies have shown that acetic anhydride can be used as an activating agent in the reaction of 1,2,4-triazin-5(2*H*)-ones **1a-c** with electron rich heterocycles (method D, Scheme 2).

Thus, heating **1a-c** with the indoles **2a-c**, the pyrroles **5a,b** and 1,3-dimethyl-2-phenylpyrazol-5-one (**8**) in acetic anhydride gives the corresponding 1-acetyl-3-aryl-6-hetaryl-1,6-dihydro-1,2,4-triazin-5(2*H*)-ones **6a-m**. It is noteworthy that *N*-methylpyrrole (**5b**) reacts under the same conditions with two moles of the 1,2,4-triazin-5(2*H*)ones **1a-c** yielding the bis-adducts **7a-c**. Compounds **1a-c** react in acetic anhydride also with 2-aminothiazoles **9a,b**. In these reactions the aminothiazole acts, after acylation of its amino group, as the carbon-nucleophile, yielding 1-acetyl-3-aryl-6-(2-acetylaminothiazolyl-5)-1,6-dihydro-1,2,4-triazin-5(2*H*)-ones **6n-s**. We have to realize that these reactions are the first examples

Table 1
6-Hetaryl-1,2,4-triazin-5(2*H*)-ones **3, 4, 6, 7**

Compound	Yield % (Method)	mp °C	Molecular Formula (Molecular weight)	Analysis		
				C	H	N
1	2	3	4	5	6	7
3a	99 (A), 71 (B), 90 (C)	210-211	C ₁₇ H ₁₄ N ₄ O (290.3)	70.33	4.86	19.30
				69.94	4.75	19.31
3b	68 (A), 58 (B), 70 (C)	205-205	C ₁₈ H ₁₆ N ₄ O (304.3)	71.04	5.29	18.50
				71.08	5.00	18.50
3c	93 (A), 65 (B)	209-210	C ₁₈ H ₁₆ N ₄ O (304.3)	71.04	5.29	18.50
3d	95 (A)	270-273	C ₁₈ H ₁₅ ClN ₄ O (338.8)	71.08	5.00	18.47
				63.81	4.46	16.54
3e	93 (A), 65 (B)	207-208	C ₁₈ H ₁₆ N ₄ O (304.3)	63.61	4.55	16.26
				71.04	5.29	18.50
				71.23	5.22	18.50

Table 1 (continued)

Compound	Yield % (Method)	mp °C	Molecular Formula (Molecular weight)	Analysis		
				C	H	N
1	2	3	4	5	6	7
3f	90 (A), 40 (13)	273-275	C ₁₇ H ₁₃ ClN ₄ O (324.8)	62.87 62.80	4.03 4.24	17.25 17.43
3g	89 (A)	218-220	C ₁₉ H ₁₈ N ₄ O (318.4)	71.68 71.37	5.69 5.71	17.60 17.55
4a	83	>320	C ₁₇ H ₁₂ N ₄ O (288.3)	70.82 70.56	4.19 4.10	19.43 19.53
4b	61	>320	C ₁₈ H ₁₄ N ₄ O (302.3)	71.51 71.53	4.66 4.82	18.53 18.69
4c	71	312-314	C ₁₈ H ₁₄ N ₄ O (302.3)	71.51 71.27	4.66 4.77	18.53 18.33
4d	61	>320	C ₁₈ H ₁₃ ClN ₄ O (336.7)	64.20 64.33	3.89 3.84	16.64 16.69
4e	60	>320	C ₁₈ H ₁₄ N ₄ O (302.3)	71.51 71.86	4.66 4.85	18.53 18.66
4h	19	>300	C ₁₅ H ₁₄ N ₄ O (266.3)	67.66 67.46	5.29 5.41	21.04 20.80
6a	88	>320	C ₁₉ H ₁₆ N ₄ O ₂ (332.4)	68.67 68.72	4.81 5.18	16.86 16.70
6b	80	287-290	C ₁₉ H ₁₅ ClN ₄ O ₂ (366.8)	62.22 62.28	4.12 4.28	15.27 15.34
6c	85	315-317	C ₂₀ H ₁₈ N ₄ O ₂ (346.4)	69.35 68.97	5.24 5.17	16.17 16.04
6d	90	297-298	C ₂₀ H ₁₈ N ₄ O ₂ (346.4)	69.35 68.97	5.24 5.06	16.17 16.35
6e	97	>300	C ₂₁ H ₂₀ N ₄ O ₂ (360.4)	69.99 69.97	5.59 5.43	15.55 15.75
6f	45	299-302	C ₂₀ H ₁₈ N ₄ O ₂ (346.4)	69.35 69.10	5.24 5.10	16.17 16.22
6g	86	298-301	C ₂₁ H ₂₀ N ₄ O ₂ (360.4)	69.99 69.67	5.59 5.44	15.55 15.74
6h	65	217-218	C ₁₅ H ₁₄ N ₄ O ₂ (282.3)	63.82 63.60	4.99 5.23	19.85 19.61
6i	60	215-217	C ₁₆ H ₁₆ N ₄ O ₂ (296.3)	64.85 64.50	5.44 5.67	18.91 18.65
6j	59	217-219	C ₁₆ H ₁₆ N ₄ O ₂ (296.3)	64.86 64.62	5.44 5.20	18.91 18.80
6k	71	209-210	C ₁₇ H ₁₈ N ₄ O ₂ (310.3)	65.79 65.61	5.84 5.84	18.05 18.08
6l	92	273-275	C ₂₂ H ₂₁ N ₅ O ₃ (403.4)	65.50 65.40	5.24 5.14	17.36 17.64
6m	90	259-260	C ₂₃ H ₂₃ N ₅ O ₃ (417.4)	66.18 66.24	5.24 5.43	16.78 17.05
6n	52	210-215	C ₁₆ H ₁₅ N ₅ O ₃ S (357.3)	53.78 53.71	4.20 4.30	19.61 19.67
6o	25	>300	C ₁₆ H ₁₄ ClN ₅ O ₃ S (391.9)	49.04 49.32	3.60 3.88	17.87 17.53
6p	45	>300	C ₁₇ H ₁₇ N ₅ O ₃ S (371.4)	54.97 54.67	4.61 4.67	18.86 18.60
6q	72	280-285	C ₂₂ H ₁₉ N ₅ O ₃ S (433.5)	60.95 60.77	4.41 4.46	16.15 16.24
6r	72	>300	C ₂₂ H ₁₈ ClN ₅ O ₃ S (467.9)	56.47 56.20	3.87 4.14	14.96 14.66
6s	75	290-295	C ₂₃ H ₂₁ N ₅ O ₃ S (447.5)	61.73 61.84	4.73 4.80	15.65 15.77
7a	80	167	C ₂₇ H ₂₅ N ₇ O ₄ (511.5)	63.39 63.39	4.92 5.18	19.16 18.98
7b	60	>300	C ₂₇ H ₂₃ Cl ₂ N ₇ O ₄ + 1 H ₂ O (598.4)	54.19 54.59	4.28 3.98	16.33 16.30
7c	69	>300	C ₂₉ H ₂₉ N ₇ O ₄ (539.6)	64.55 64.47	5.41 5.43	18.17 18.07

for using aminothiazoles as carbon-nucleophiles in the nucleophilic aromatic addition to heterocycles.

The spectral data of the compounds obtained (Tables 2 and 3) are in full agreement with the proposed structures. The position (N_1) of the acetyl group in the dihydro-1,2,4-triazin-5(2*H*) ones 6 is provided by the following facts: in the 1H nmr spectra of compounds 2 the signal for the

proton in the 6-position is observed as a broadened singlet or doublet around $\delta = 4.8$, due to spin-spin-coupling with the N_1 -proton which gives a signal around $\delta = 7$. The spin-spin coupling was proved by double resonance experiments. In the 1H nmr spectra of the acetylated dihydro-1,2,4-triazin-5(2*H*)-ones 6, 7 the signal for 6-H is observed as a narrow singlet between $\delta = 5.7 - 6.7$ and no signal for

Table 2
 1H -NMR Data for 3-Aryl-6-hetaryl-1,2,4-triazin-5(2*H*)ones 3, 4, 6, 7

Compound	Chemical shifts (80 MHz, 300 MHz [a])				
	Ar 2	Het 3	6-H 4	N_1 H(AC) 5	N_2 H 6
3a [a]	6.98-7.03 (m, 1H), 7.08-7.13 (m, 1H), 7.23 (d, J = 2, 3 Hz, 1H), 7.34-7.44 (m, 4H), 7.67 (d, J = 7.8 Hz, 1H), 7.77-7.80 (m, 2H), 11.02 (br s, 1H)		4.87 (br s, 1H)	7.53 (br s, 1H)	10.85 (s, 1H)
3b [a]	2.33 (s, 3H), 6.97-7.02 (m, 1H), 7.07-7.13 (m, 1H), 7.20-7.24 (m, 3H), 7.38 (d, J = 8.0 Hz, 1H), 7.65-7.69 (m, 3H), 11.02 (br s, 1H)		4.85 (d, J = 1.2 Hz, 1H)	7.44 (br s, 1H)	10.85 (s, 1H)
3c [a]	2.36 (s, 3H), 6.87-6.92 (m, 1H), 6.99-7.02 (m, 1H), 7.28 (d, J = 10.9 Hz, 1H), 7.40-7.46 (m, 4H), 7.79-7.82 (m, 2H), 11.00 (br s, 1H)		4.76 (d, J = 2.1 Hz, 1H)	7.19 (d, J = 2.1 Hz, 1H)	10.83 (s, 1H)
3d [a]	7.49 (d, J = 8, 7 Hz, 2H), 7.82 (d, J = 8, 7 Hz, 2H)	2.35 (s, 3H), 6.86-6.91 (m, 1H), 6.96-7.00 (m, 1H), 7.27 (d, J = 8.0 Hz, 1H), 7.44 (d, J = 7.8 Hz, 1H), 11.00 (br s, 1H)	4.77 (br s, 1H)	7.26 (br s, 1H)	10.85 (s, 1H)
3e [a]	7.39-7.44 (m, 3H), 7.78-7.81 (m, 2H)	3.75 (s, 3H), 7.02-7.07 (m, 1H), 7.14-7.20 (m, 1H), 7.24 (s, 1H), 7.68 (d, J = 7.8 Hz, 1H), 11.02 (br s, 1H)	4.87 (d, J = 1.2 Hz, 1H)	7.52 (br s, 1H)	10.85 (s, 1H)
3f [a]	7.48 (d, J = 8, 7 Hz, 2H), 7.80 (d, J = 8, 7 Hz, 2H)	6.97-7.02 (m, 1H), 7.07-7.13 (m, 1H), 7.23 (d, J = 2.3 Hz, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 11.02 (br s)	4.89 (br s, 1H)	7.60 (br s, 1H)	10.48 (s, 1H)
3g [a]	2.33 (s, 3H), 2.35 (s, 3H), 6.85-6.91 (m, 1H), 6.95-7.01 (m, 1H), 7.21-7.28 (m, 3H), 7.44 (d, J = 7.8 Hz, 1H), 7.68-7.71 (d, J = 8.2 Hz, 2H), 10.98 (b. s, 1H)		4.73 (br s, 1H)	7.08 (br s, 1H)	10.75 (s, 1H)
4a [a]	7.60-7.67 (m, 3H), 8.14-8.17 (m, 2H)	7.18-7.27 (m, 2H), 7.51-7.54 (m, 1H), 8.45 (d, J = 6.9 Hz, 1H), 8.87 (br s, 1H), 11.78 (br s, 1H)	-	-	14.20 (br s, 1H)
4b [a]	2.42 (s, 3H), 7.42 (d, J = 8.2 Hz, 2H), 8.06 (d, J = 8.2 Hz, 2H)	7.18-7.22 (m, 2H), 7.51-7.54 (m, 1H), 8.46 (d, J = 6.9 Hz, 1H), 8.85 (d, J = 3.0 Hz, 1H), 11.77 (br s, 1H)	-	-	14.20 (br s, 1H)
4c [a]	7.60-7.68 (m, 3H), 8.14-8.16 (m, 2H)	2.52 (s, 3H), 7.00-7.11 (m, 2H), 7.34-7.36 (m, 1H), 7.68 (d, J = 6.9 Hz, 1H), 11.60 (br s, 1H)	-	-	14.20 (br s, 1H)
4d [a]	7.70 (d, J = 8.6 Hz, 2H), 8.16 (d, J = 8.6 Hz, 2H)	2.50 (s, 3H), 6.99-7.10 (m, 2H), 7.34-7.37 (m, 1H), 7.67-7.69 (m, 1H), 11.51 (br s, 1H)	-	-	14.20 (br s, 1H)
4e	7.62-7.68 (m, 3H), 8.14-8.17 (m, 2H)	3.93 (s, 3H), 7.23-7.35 (m, 2H), 7.57-7.59 (m, 1H), 8.48-8.50 (m, 1H), 8.87 (s, 1H)	-	-	14.20 (br s, 1H)
4h [a]	2.42 (s, 3H), 7.42 (d, J = 8.2 Hz, 2H), 8.03 (d, J = 8.2 Hz, 2H)	3.99 (s, 3H), 6.13-6.25 (m, 1H), 7.06 (m, 1H), 7.39-7.42 (m, 1H)	7.05-	--	14.05 (br s, 1H)
6a	6.80-8.20 (m, 10H), 11.00 (br s, 1H)		6.33 (s, 1H)	2.32 (s, 3H)	11.70 (br s, 1H)
6b	6.90-8.12 (m, 9H), 11.00 (br s, 1H)		6.30 (s, 1H)	2.30 (s, 3H)	11.70 (br s, 1H)
6c	2.40 (s, 3H), 6.90-7.92 (m, 9H), 11.00 (br s, 1H)		6.35 (s, 1H)	2.30 (s, 3H)	11.70 (br s, 1H)
6d [a]	7.47-7.56 (m, 3H), 7.93-7.96 (m, 2H)	3.70 (s, 3H), 7.04-7.10 (m, 1H), 7.15-7.20 (m, 2H), 7.39 (d, J = 8.2 Hz, 1H), 7.73 (d, J = 7.8 Hz, 1H)	6.70 (s, 1H)	2.34 (s, 3H)	11.60 (br s, 1H)
6e [a]	2.36 (s, 3H), 7.31 (d, J = 8.1 Hz, 2H), 7.84 (d, J = 8.1 Hz, 2H)	3.69 (s, 3H), 7.04-7.09 (m, 1H), 7.16-7.20 (m, 2H), 7.39 (d, J = 8.2 Hz, 1H), 7.72 (d, J = 7.8 Hz, 1H)	6.28 (s, 1H)	2.32 (s, 3H)	11.61 (br s, 1H)

Table 2 (continued)

Compound 1	Chemical shifts (80 MHz, 300 MHz [a])				
	Ar 2	Het 3	6-H 4	N ₁ H(AC) 5	N ₂ H 6
6f [a]	7.54-7.56 (m, 3H), 7.97-8.00 (m, 2H)	2.49 (s, 3H), 6.76-6.81 (m, 1H), 6.92-6.98 (m, 1H), 7.17 (d, J = 7.9 Hz, 1H), 7.25 (d, J = 8.0 Hz, 1H), 11.65 (s, 1H)	6.17 (s, 1H)	2.26 (s, 3H)	11.14 (br s, 1H)
6g [a]	2.38 (s, 3H), 7.35 (d, J = 8.1 Hz, 2H), 7.88 (d, J = 8.1 Hz, 2H)	2.48 (s, 3H), 6.76-6.81 (m, 1H), 6.92-6.97 (m, 1H), 7.16 (d, J = 7.9 Hz, 1H), 7.25 (d, J = 8.0 Hz, 1H), 11.59 (s, 1H)	6.16 (s, 1H)	2.24 (s, 3H)	11.10 (br s, 1H)
6h [a]	7.46-7.56 (m, 3H), 7.89-7.92 (m, 2H)	5.78 (s, 1H), 5.87-5.90 (m, 1H), 6.64-6.67 (m, 1H), 10.97 (br s, 1H)	6.02 (s, 1H)	2.31 (s, 3H)	11.60 (br s, 1H)
6i [a]	2.35 (s, 3H), 7.30 (d, J = 8.2 Hz, 2H), 7.80 (d, J = 8.2 Hz, 2H)	5.75-5.78 (m, 1H), 5.89-5.94 (m, 1H), 6.63-6.66 (m, 1H), 10.96 (br s, 1H)	6.0216 (s, 1H)	2.30 (s, 3H)	11.54 (br s, 1H)
6j [a]	7.50-7.56 (m, 3H), 7.92-7.95 (m, 2H)	3.76 (s, 3H), 5.78-5.80 (m, 1H), 5.85-5.87 (m, 1H), 6.72-6.74 (m, 1H)	6.07 (s, 1H)	2.31 (s, 3H)	11.70 (br s, 1H)
6k [a]	2.37 (s, 3H), 7.32 (d, J = 8.2 Hz, 2H), 7.83 (d, J = 8.2 Hz, 2H)	3.74 (s, 3H), 5.75-5.77 (m, 1H), 5.83-5.86 (m, 1H), 6.71-6.72 (m, 1H)	6.06 (s, 1H)	2.29 (s, 3H)	11.65 (br s, 1H)
6l [a]	2.45 (s, 3H), 3.11 (s, 3H), 7.23-7.31 (m, 3H), 7.41-7.50 (m, 5H), 7.84-7.87 (m, 2H)		5.71 (s, 1H)	2.27 (s, 3H)	11.42 (br s, 1H)
6m [a]	2.35 (s, 3H), 2.44 (s, 3H), 3.10 (s, 3H), 7.22-7.31 (m, 5H), 7.41-4.47 (m, 2H), 7.76 (d, J = 8.1 Hz, 2H)		5.70 (s, 1H)	2.26 (s, 3H)	11.39 (br s, 1H)
6n	7.30-8.10 (m, 5H)	2.10 (s, 3H), 7.30 (d, J = 1.2 Hz, 1H), 12.10 (br s, 1H)	6.20 (d, J = 1.2 Hz)	2.30 (s, 3H)	11.70 (br s, 1H)
6o	7.56 (d, J = 8.1 Hz, 2H), 8.05 (d, J = 8.1 Hz, 2H)	2.12 (s, 3H), 7.20 (d, J = 1.2 Hz, 1H), 12.20 (br s, 1H)	6.23 (d, J = 1.2 Hz)	2.31 (s, 3H)	11.70 (br s, 1H)
6p	2.40 (s, 3H), 7.33 (d, J = 8.0 Hz, 2H), 7.80 (d, J = 8.0 Hz, 2H)	2.10 (s, 3H), 7.30 (d, J = 1.2 Hz, 1H), 12.10 (br s, 1H)	6.20 (d, J = 1.2 Hz)	2.30 (s, 3H)	11.70 (br s, 1H)
6q	2.10 (s, 3H), 7.30-8.10 (m, 10H), 12.30 (br s, 1H)		6.50 (s, 1H)	2.35 (s, 3H)	11.70 (br s, 1H)
6r	2.10 (s, 3H), 7.20-8.10 (m, 9H), 12.30 (br s, 1H)		6.52 (s, 1H)	2.30 (s, 3H)	11.70 (br s, 1H)
6s	2.10 (s, 3H), 2.40 (s, 3H), 7.20-8.15 (m, 9H), 12.30 (br s, 1H)		6.50 (s, 1H)	2.30 (s, 3H)	11.70 (br s, 1H)
7a	7.30-8.15 (m, 10H)	3.83 (s, 3H), 5.75 (s, 2H)	6.17 (s, 2H)	2.35 (s, 6H)	11.70 (br s, 2H)
7b	7.50 (d, J = 8.1 Hz, 4H), 8.00 (d, J = 8.1 Hz, 4H)	3.95 (s, 3H), 5.70 (s, 2H)	6.15 (s, 2H)	2.35 (s, 6H)	11.70 (br s, 2H)
7c	2.34 (s, 6H), 7.28 (d, J = 8.2 Hz, 4H), 7.77 (d, J = 8.2 Hz, 4H)	3.90 (s, 3H), 5.67 (s, 2H)	6.08 (s, 2H)	2.28 (s, 3H)	11.70 (br s, 2H)

Table 3

IR and MS Data for 3-Aryl-6-hetaryl-1, 2, 4-triazin-5(2H)-ones 3, 4, 6, 7

Compound 1	IR	MS, nm/z(%), 70 eV
	ν_{CO} 2	3
3a	1690	290 (100) [M ⁺], 262 (26), 261 (41), 173 (19), 157 (64) [HetCHO ⁺], 143 (17), 129 (52), 117 (86), 104 (41), 90 (25), 89 (19), 77 (23)
3b	1710	304 (80) [M ⁺], 276 (38), 275 (67), 159 (23), 157 (100) [HetCHO ⁺], 144 (18), 143 (27), 130 (17), 129 (85), 118 (69), 117 (82), 116 (26), 91 (25), 90 (41), 89 (32)
3c	1715	304 (55) [M ⁺], 276 (41), 275 (17), 171 (95) [HetCHO ⁺], 157 (25), 143(100), 142 (18), 131 (60), 130 (80), 121 (23), 113 (60), 112 (25)
3d	1715	338 (15) [M ⁺], 207 (33), 180 (24), 155 (20), 140 (27), 139 (21), 138 (100), 137 (39), 130 (42), 111 (20), 103 (32), 75 (33)
3e	1710	304 (100) [M ⁺], 276 (32), 275 (37), 171 (67) [HetCHO ⁺], 143 (41)
3f	1705	324 (19) [M ⁺], 295 (18), 207 (22), 180 (19), 157 (34) [HetCHO ⁺], 143 (17), 129 (52), 117 (86), 104 (41), 90 (25), 89 (19), 77 (23)
3g	1710	318 (59) [M ⁺], 290 (33), 289 (30), 171 (100) [HetCHO ⁺], 157 (22), 156 (37), 143 (92), 135 (27), 131 (58), 130 (74), 118 (59)

Table 3 (continued)

Compound	IR ν_{CO}	MS, nm/z(%, 70 eV)	
		1	3
4a	1600	288 (92) [M ⁺], 157 (67) [HetCNNH ⁺], 142 (100) [HetCN ⁺], 129 (15), 128 (15), 115 (20), 104 (23), 77 (27)	
4b	1600	302 (100) [M ⁺], 161 (21), 157 (65) [HetCNNH ⁺], 142 (98) [HetCN ⁺], 118 (21)	
4c	1590	302 (84) [M ⁺], 171 (40) [HetCNNH ⁺], 157 (41), 156 (100) [HetCN ⁺], 155 (42), 77 (18)	
4d	1600	338 (17), 336 (54) [M ⁺], 171 (49) [HetCNNH ⁺], 157 (58), 156 (100) [HetCN ⁺], 155 (42)	
4e	1590	302 (95) [M ⁺], 171 (64) [He CNNH ⁺], 157 (18), 156 (100) [HetCN ⁺], 155 (22), 142 (16), 77 (18)	
4h	1660	266 (100) [M ⁺], 265 (50), 121 (84), 118 (64), 106 (90), 93 (37), 91 (45), 65 (74)	
6a	1660, 1700	332 (67) [M ⁺], 289 (100), 274 (33), 261 (28), 246 (15), 245 (16), 171 (15), 157 (49), 143 (63), 127 (80), 104 (49)	
6b	1650, 1700	368 (24), 366 (76) [M ⁺], 326 (20), 325 (50), 324 (56), 323 (100), 308 (30), 157 (31), 129 (48)	
6c	1660, 1700	346 (42) [M ⁺], 290 (100), 288 (27), 275 (38), 157 (42), 143 (49), 129 (86), 118 (54), 102 (22), 91 (19), 89 (15)	
6d	1672, 1702	346 (100) [M ⁺], 303 (89), 288 (48), 260 (25), 171 (30), 157 (43), 143 (57), 127 (80), 104 (19), 77 (21)	
6e	1671, 1702	360 (94) [M ⁺], 317 (100), 302 (55), 274 (21), 171 (30), 157 (42), 143 (67), 118 (22), 91 (15)	
6f	1670, 1700	346 (100) [M ⁺], 303 (60), 288 (19), 174 (30), 171 (36), 143 (78), 131 (22), 130 (52), 104 (24), 77 (28)	
6g	1671, 1702	360 (100) [M ⁺], 317 (82), 303 (21), 302 (28), 188 (63), 171 (48), 157 (40), 143 (73), 131 (27), 130 (45), 118 (30), 91 (16)	
6h	1670, 1700	282 (44) [M ⁺], 239 (100), 224 (16), 147 (73), 107 (51), 104 (57), 93 (39), 79 (71), 77 (40)	
6i	1672, 1702	296 (36) [M ⁺], 253 (100), 238 (15), 161 (82), 118 (66), 98 (41), 91 (36), 78 (73)	
6j	1670, 1702	296 (44) [M ⁺], 253 (100), 121 (44), 117 (20), 114 (16), 93 (34), 77 (16)	
6k	1672, 1702	310 (45) [M ⁺], 267 (100), 121 (52), 118 (34), 107 (28), 95 (63), 75 (21), 74 (22)	
6l	1660, 1671, 1702	403 (31) [M ⁺], 360 (100), 258 (19), 257 (22), 216 (43), 215 (52), 214 (25), 201 (25), 77 (24)	
6m	1660, 1672, 1702	417 (36) [M ⁺], 374 (100), 258 (42), 257 (50), 216 (78), 215 (99), 214 (42), 201 (44), 118 (22), 91 (22), 77(25)	
6n	1660, 1670, 1710	357 (28) [M ⁺], 314 (100), 272 (27), 140 (22), 104 (32), 77 (21)	
6o	1650, 1670, 1700	393 (15), 391 (22), 350 (42), 348 (100), 308 (15), 306 (30)	
6p	1660, 1670, 1715	371 (15) [M ⁺], 328 (100), 276 (41), 140 (22), 188 (27), 173 (15), 118 (22)	
6q	1660, 1670, 1700	433 (62) [M ⁺], 390 (100), 348 (38), 316 (16), 216 (24), 146 (16), 104 (32), 77 (27)	
6r	1660, 1675, 1715	469 (16), 467 (29), 426 (29), 424 (100), 384 (21), 382 (60)	
6s	1665, 1680, 1710	447 (43) [M ⁺], 404 (100), 362 (30), 216 (29), 118 (19)	
7a	1630, 1670	511 (60) [M ⁺], 468 (90), 424 (10), 411 (43), 410 (21), 378 (10), 300 (59), 258 (100), 174 (27), 104 (30), 77 (27)	
7b	1650, 1670		
7c	1630, 1690	539 (35) [M ⁺], 496 (100), 453 (24), 452 (27), 430 (20), 429 (52), 428 (30), 309 (26), 267 (78)	

N₁-H can be found. The signals for the N₂-protons can be observed in all compounds between $\delta = 10$ -11.

EXPERIMENTAL

Melting points (uncorrected) were obtained on a Kofler plate. The ¹H-nmr were observed on a Bruker WM 300 (300 MHz) or on a Bruker WP 80 (80 MHz) with TMS as the internal standard. The mass spectra were obtained on a Varian MAT-311A with a Teknivent V1 data system. The ir spectra were obtained as potassium bromide pellets using a Perkin-Elmer IR spectrometer Model 297.

General Procedure for the Preparation of 3-Aryl-6-indolyl-1,6-dihydro-1,2,4-triazin-5(2H)-ones **3a-g** (Tables 1-3).

Method A.

3-Aryl-1,2,4-triazin-5(2H)-ones **1a-c** (5 mmoles) and indoles **2a-c** (5.5 mmoles) in chloroform (5 ml) and trifluoroacetic acid (1 ml) were stirred at room temperature for 2-6 hours. The precipitate was filtered and washed with chloroform and recrystallized from methanol.

Method B.

3-Aryl-1,2,4-triazin-5(2H)-ones **1a-c** (5 mmoles) and indoles **2a-c** (5.5 mmoles) were refluxed in acetic acid (4 ml) for 2-4 hours. The solvent was removed under vacuum. The residue was stirred with water, filtered and recrystallized from methanol.

Method C.

3-Aryl-1,2,4-triazin-5(2H)-ones **1a-c** (5 mmoles) and indoles **2a-c** (5.5 mmoles) were refluxed in butanol (10 ml) for 6 days. The solvent was removed under vacuum. The residue was washed with ether and recrystallized from methanol.

General Procedure for the Preparation of 3-Aryl-6-indolyl-1,2,4-triazin-5(2H)-ones **4a-e** (Tables 1-3).

The corresponding 3-aryl-6-indolyl-1,6-dihydro-1,2,4-triazin-5(2H)-one **3a-e** (1 mmole) was refluxed in DMF (10 ml) for 8-10 hours with bubbling air through the solution. The solvent was removed under vacuum, the residue stirred with water, filtered and recrystallized from methanol.

3-Tolyl-6-(1-methylpyrrolyl-2)-1,2,4-triazin-5(2H)-one (**4h**).

3-Tolyl-1,2,4-triazin-5(2H)-one (**1c**) (867 mg, 5 mmoles) and *N*-methylpyrrole (**5b**) (810 mg, 10 mmoles) were refluxed in butanol (10 ml) for 6 days. The solvent was removed under vacuum, the residue washed with ether and recrystallized from methanol.

General Procedure for the Preparation of 1-Acetyl-3-aryl-6-hetaryl-1,6-dihydro-1,2,4-triazin-5(2H)-ones **6a-q** (Tables 1-3).

Method D.

The corresponding 3-aryl-1,2,4-triazin-5(2H)-one **1a-c** (5 mmoles) was refluxed with the indoles **2a-c**, pyrroles **5a,b**, 1,3-dimethyl-2-phenylpyrazol-5-one (**8**) or the aminothiazoles

9a,b (5.5 mmoles) in acetic anhydride (7 ml) for 2-2.5 hours. The precipitate was filtered, washed with ether and recrystallized from methanol.

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