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Transformations of 1,2,4-Triazines in Reactions with Nucleophiles: V.* S_N^H and *ipso*-Substitution in the Synthesis and Transformations of 5-Cyano-1,2,4-triazines**

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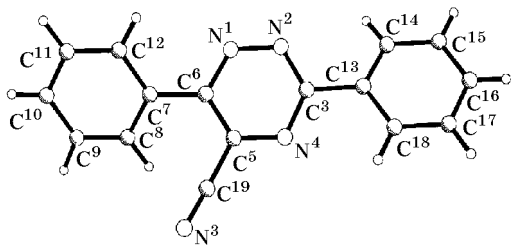
Abstract—The scope of functionalization of 1,2,4-triazines can be considerably extended via successive nucleophilic substitution of hydrogen (S_N^H) and *ipso*-substitution. A convenient procedure has been developed for direct cyanation of 1,2,4-triazine 4-oxides with acetone cyanohydrin in the presence of triethylamine. The cyano group in the resulting 5-cyano-1,2,4-triazines is readily replaced by reactions with various aliphatic alcohols and amines.

The cyano group in 5-cyano-1,2,4-triazines is readily replaced by the corresponding groups in reactions with CH acids, organomagnesium compounds, alcohols, and water; therefore, these reactions can be used for functionalization of 1,2,4-triazines [2–4]. However, their wide application is limited because of difficulties in the preparation of initial cyano-1,2,4-triazines. The known procedures for cyanation of 1,2,4-triazines include a number of intermediate stages: introduction of a halogen atom and subsequent halogen replacement by cyano group [2] or hydroxyiminomethyl group and dehydration of the latter [4]. Only one example of direct cyanation in the 1,2,4-triazine series was reported: the formation of 5-cyano-6-methyl-3-phenyl-1,2,4-triazine by the action of dry hydrogen cyanide on 6-methyl-3-phenyl-1,2,4-triazine [5]. We briefly reported in [6] on a method which allowed us to smoothly accomplish nucleophilic substitution of hydrogen by cyano group in 6-phenyl-1,2,4-triazine 4-oxides with generation of CN^- ion *in situ*.

The present communication describes the results of our studies which extend the scope of the reactions of 1,2,4-triazine 4-oxides with cyanide ion and its synthetic equivalents; also, the reactivity and other properties of 5-cyano-1,2,4-triazines are reported. By treatment of substituted 1,2,4-triazine 4-oxides **Ia**–**Ig** with acetone cyanohydrin in the presence of triethylamine we obtained in high yields (in most cases, nearly quantitative) the corresponding 5-cyano-1,2,4-triazines **IIa**–**IIg** (Scheme 1). The reaction occurs exclusively at position *5* of the 1,2,4-triazine ring even when the substrate has no substituent at C^3 and is accompanied by loss of the *N*-oxide moiety.

The structure of 5-cyano-1,2,4-triazines **II** was proved by NMR spectroscopy and mass spectrometry (Table 2). The physical parameters of 5-cyano-3,6-diphenyl-1,2,4-triazine (**IIc**) coincided with those reported in [2]. The IR spectrum of **IId** contained no absorption band typical of C≡N stretching vibrations (2200–2260 cm^{-1}), but a strong band at 1400 cm^{-1} was present. An analogous pattern was observed in [3] for compound **IIc**. Therefore, we performed X-ray analysis of 5-cyano-3,6-diphenyl-1,2,4-triazine (**IIc**). The central triazine ring plane in molecule **IIc** form



Molecular structure of 5-cyano-3,6-diphenyl-1,2,4-triazine (**IIc**) according to the X-ray diffraction data.

* For communication IV, see [1].

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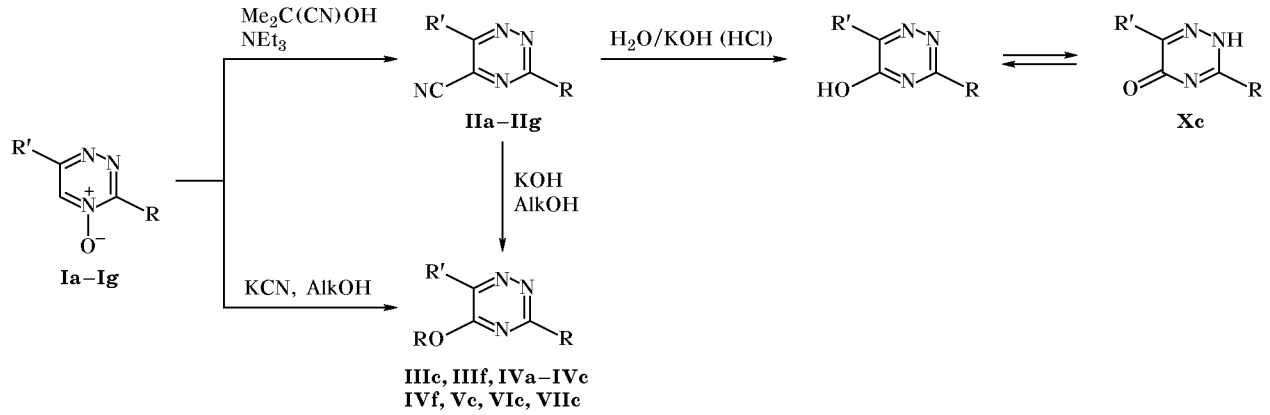
Scheme 1.



I–**XI**, R = H, R′ = Ph (**a**); R = Me, R′ = Ph (**b**); R = R′ = Ph (**c**); R = 4-ClC_6H_4, R′ = Ph (**d**); R = 4-$O_2NC_6H_4$, R′ = Ph (**e**); R = Ph, R′ = 4-ClC_6H_4 (**f**); R = R′ = 4-ClC_6H_4 (**g**); **III**, Alk = Me; **IV**, Alk = Et; **V**, Alk = *i*-Pr; **VI**, Alk = Bu; **VII**, Alk = $HOCH_2CH_2$.

dihedral angles of 11.1 and 48.2°, respectively, with the benzene rings in positions *3* and *6*. The C≡N bond is shorter (1.129 Å) than the standard one (1.157 Å), presumably due to conjugation with the π-deficient 1,2,4-triazine ring (Tables 3, 4; see figure). This fact is likely to be responsible for the observed IR spectral patterns of 5-cyano-1,2,4-triazines **II**.

The reaction leading to 5-cyano-1,2,4-triazines **II** is an S_N^H process [7] which can be described by a two-step mechanism. In the first stage cyanide ion generated *in situ* from acetone cyanohydrin adds at C^5 of the 1,2,4-triazine ring to form σ^H-adduct **A**, as in the reactions of 1,2,4-triazine 4-oxides with aromatic C-nucleophiles [8]. The second stage is autoaromatization through elimination of water molecule. Obviously, the dehydration process follows E1cb-like mechanism. Electron-acceptor cyano group at C^5 increases acidity of the 5-H proton, and basic medium facilitates its abstraction. The subsequent elimination of hydroxide ion from anion **B** gives aromatic products **II** (Scheme 2).

We also made an attempt to use potassium cyanide in methanol or ethanol as cyanating agent. However, the reactions with 1,2,4-triazine 4-oxides **Ia**–**Id** and **If** led to formation of the corresponding 5-methoxy- or 5-ethoxy-1,2,4-triazines **IIIc**, **IIIf**, **IVa**–**IVc**, and **IVf** in high yields (Scheme 1). Obviously, the first stage in the reaction of **I** with potassium cyanide is formation of 5-cyano-1,2,4-triazines **II**, but the subsequent fast replacement of the cyano group by the alcohol residue yields 5-alkoxy derivatives **III** and **IV**. Thus, treatment of preliminarily prepared 5-cyano-1,2,4-triazines **II** with methanol or ethanol in the presence of a catalytic amount of KOH afforded the same 5-alkoxy-1,2,4-triazines **III** and **IV** (Scheme 1).

This finding led us to develop a procedure for synthesizing 5-alkoxy-1,2,4-triazines, which may be illustrated using 5-cyano-3,6-diphenyl-1,2,4-triazine (**IIc**) as an example. Heating of compound **IIc** in boiling 2-propanol or butanol containing a catalytic amount of the corresponding sodium alkoxide resulted in replacement of the cyano group and formation of 5-isopropoxy- and 5-butoxy-3,6-diphenyl-1,2,4-triazines **Vc** and **VIc**. The spectral parameters of alkoxy-1,2,4-triazines **IIIc**, **IIIf**, **IVa**–**IVc**, **IVf**, **Vc**, and **VIc** (Table 2) are consistent with their structure. The data for 5-methoxy-6-phenyl-1,2,4-triazine (**IIIa**) and 5-ethoxy-3,6-diphenyl-1,2,4-triazine (**IVc**) coincided with those given in [9, 2].

Analogous reactions occur with polyatomic alcohols. By heating of 5-cyano-3,6-diphenyl-1,2,4-triazine (**IIc**) in a 1:1 mixture of DMF with ethylene glycol we obtained 5-(2-hydroxyethoxy)-3,6-diphenyl-1,2,4-triazine (**VIIc**) (Scheme 1; Tables 1, 2). Under

Scheme 2.

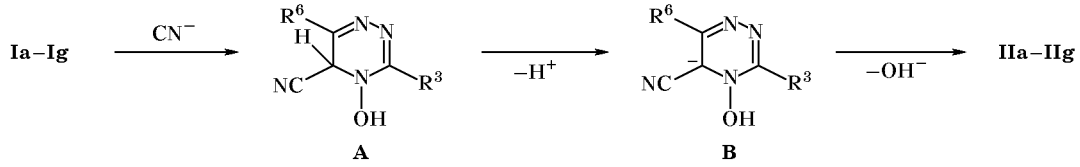
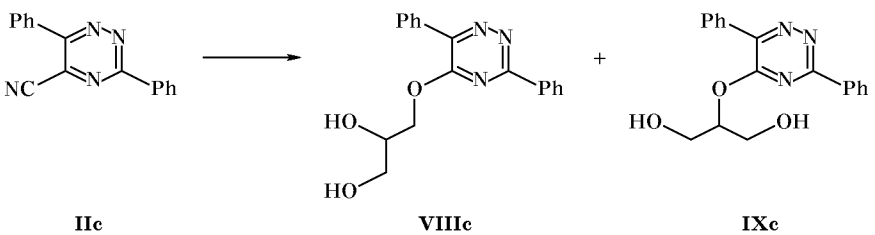


Table 1. Yields, melting points, and elemental analyses of compounds **II**–**XXI**

Comp. no.	Yield, %	mp, °C	Found, %			Formula	Calculated, %		
			C	H	N		C	H	N
IIa	75	86	65.88	3.39	30.69	$C_{10}H_6N_4$	65.93	3.32	30.75
IIb	80	88	67.45	4.22	28.46	$C_{11}H_8N_4$	67.34	4.11	28.55
IIc	95	163 [2]	74.30	3.98	21.56	$C_{16}H_{10}N_4$	74.41	3.90	21.69
IId	97	178	65.74	3.01	19.23	$C_{16}H_9ClN_4$	65.65	3.10	19.14
IIe	100	174	63.30	3.12	22.95	$C_{16}H_9N_5O_2$	63.37	2.99	23.09
IIf	95	164	65.46	3.33	19.01	$C_{16}H_9ClN_4$	65.65	3.20	19.14
IIg	100	182	58.80	2.38	17.01	$C_{16}H_8Cl_2N_4$	58.74	2.46	17.12
IIIc	85	117 [9]	73.06	5.09	15.89	$C_{16}H_{13}N_3O$	72.99	4.98	15.96
IIIf	95	143	64.48	4.18	14.02	$C_{16}H_{12}ClN_3O$	64.54	4.06	14.11
IVa	77	82	65.72	5.67	20.79	$C_{11}H_{11}N_3O$	65.66	5.51	20.88
IVb	80	74	66.85	6.20	19.60	$C_{12}H_{13}N_3O$	66.96	6.09	19.52
IVc	76	103 [2]	73.47	5.61	15.24	$C_{17}H_{15}N_3O$	73.63	5.45	15.15
IVf	90	155	65.33	4.61	13.41	$C_{17}H_{14}ClN_3O$	65.49	4.53	13.48
Vc	79	101	74.15	5.99	14.39	$C_{18}H_{17}N_3O$	74.21	5.88	14.42
VIc	93	130	67.32	5.48	12.18	$C_{19}H_{18}ClN_3O$	67.16	5.34	12.37
VIIc	95	129	69.45	5.07	14.09	$C_{17}H_{15}N_3O_2$	69.61	5.15	14.33
Xc	81	273 [10]	72.05	4.61	16.92	$C_{15}N_{11}N_3O$	72.28	4.45	16.86
XIc	80	218 [11]	72.48	4.96	22.39	$C_{15}H_{12}N_4$	72.56	4.87	22.57
XIIc	85	155	73.64	5.80	20.11	$C_{17}H_{16}N_4$	73.89	5.84	20.27
XIIIc	92	154	71.99	6.00	22.23	$C_{19}H_{19}N_5$	71.90	6.03	22.06
XIVc	93	140	75.40	5.87	18.68	$C_{19}H_{18}N_4$	75.47	6.00	18.53
XVc	90	139	76.02	6.44	17.54	$C_{20}H_{20}N_4$	75.92	6.37	17.71
XVIc	91	163	71.61	5.82	17.69	$C_{19}H_{18}N_4O$	71.68	5.70	17.60
XVIIc	52	145	78.19	5.28	16.66	$C_{22}H_{18}N_4$	78.08	5.36	16.56
XVIIIc	60	118	68.38	5.59	16.93	$C_{19}H_{18}N_4O_2$	68.25	5.43	16.76
XIXc	95	141	70.01	5.50	19.09	$C_{17}H_{16}N_4O$	69.85	5.52	19.16
XXc	91	170	70.45	6.00	18.02	$C_{18}H_{18}N_4O$	70.57	5.92	18.29
XXIc	94	60	71.29	6.11	17.42	$C_{19}H_{20}N_4O$	71.23	6.29	17.49

the same conditions, the reaction of **IIc** with glycerol gave an inseparable mixture of two isomers, 5-(2,3-dihydroxy-1-propoxy)- and 5-(1,3-dihydroxy-2-propoxy)-3,6-diphenyl-1,2,4-triazines **VIIIc** and **IXc** (Scheme 3), which was analyzed by ^{1}H NMR spectroscopy. The γ-methylene group in the glycerol fragment of **VIIIc** gives rise to a two-proton doublet of doublets (^3J = 5.5 Hz), the CH signal is a one-proton multiplet, nonequivalent protons of the α-methylene group appear as one-proton doublets of doublets (^2J = 11, ^3J = 6 Hz and ^2J = 11, ^3J = 4 Hz, respectively), the γ-OH group gives a doublet with ^3J = 5.5 Hz), and signal from the β-hydroxy proton is a triplet with ^3J = 5.5 Hz. This spectral pattern suggests that substitution of the cyano group occurs as a result of nucleophilic attack by the primary hydroxy group of

Scheme 3.



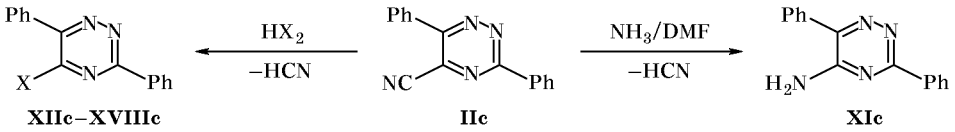
IIc **VIIIc** **IXc**

Table. 2 ^{1}H NMR spectra of compounds **II**–**IX** and **XI**–**XXI** in DMSO-d_6

Comp. no.	Chemical shifts δ, ppm (*J*, Hz)		Comp. no.	Chemical shifts δ, ppm (*J*, Hz)	
	X, OR	R, R′		X, OR	R, R′
IIa		7.6 m (2H), 8.0 m (3H), 10.09 s (3-H)	**VIIIc**	11, ^3J = 6), 4.75 d.d (1H, J^2 = 11, ^3J = 4), 4.80 d (1H, ^3J = 5.5, OH), 5.09 d (1H, ^3J = 5.5, OH)	
IIb		2.93 s (3H), 7.6 m (2H), 8.0 m (3H)			
IIc		7.6–7.7 m (6H), 8.0–8.1 m (2H), 8.5 m (2H)	**IXc**	3.80 m (4H), 4.9 t (2H, ^3J = 5.5, OH); 5.65 m (1H)	7.6 m (6H), 8.1 m (2H), 8.5 m (2H)
IId		7.50 m (3H), 7.65 m (2H), 8.09 m (4H)			
IIe		7.7 m (3H), 8.2 m (2H), 8.45 m (2H), 8.80 m (2H)	**XIc**	7.4 br.s (2H, NH_2)	7.6 m (6H), 7.75 m (2H), 8.42 m (2H)
IIf		7.68 m (3H), 7.80 m (2H), 8.09 m (2H), 8.50 m (2H)	**XIIc**	2.94 s (6H)	7.5–7.7 m (8H), 8.41 m (2H)
IIg		7.56 m (2H), 7.63 m (2H), 8.09 m (2H), 8.53 m (2H)	**XIIIc**	2.69 m (2H), 3.40 m (2H)	7.55 m (6H), 7.78 m (2H), 8.41 m (2H)
IIIc	4.17 s (3H)	7.6 m (6H), 8.1 m (2H), 8.5 m (2H)	**XIVc**	1.81 m (4H), 3.20 m (4H)	7.5 m (8H), 8.45 m (2H)
IIIf	4.15 s (3H)	7.6 m (5H), 8.1 m (2H), 8.5 m (2H)	**XVc**	1.52 m (6H), 3.44 m (4H)	7.60 m (6H), 7.77 m (2H), 8.42 m (2H)
IVa	1.40 t (3H, ^3J = 7), 4.56 q (2H, ^3J = 7)	7.4–8.1 m (5H), 9.18 s (3-H)	**XVIc**	3.46 m (4H), 3.61 m (4H)	7.60 m (6H), 7.78 m (2H), 8.42 m (2H)
IVb	1.38 t (3H, ^3J = 7), 4.52 q (2H, ^3J = 7)	2.66 s (3H), 7.4–8.1 m (5H)	**XVIIc**	4.69 d (2H, ^3J = 6), 7.2–7.5 m (5H), 8.07 br.t (1H, ^3J = 6, NH)	7.55 m (6H), 7.75 m (2H), 8.38 m (2H)
IVc	1.46 t (3H, ^3J = 7), 4.68 q (2H, ^3J = 7)	7.4–8.6 m (10H)			
IVf	1.45 t (3H, ^3J = 7), 4.62 q (2H, ^3J = 7)	7.6 m (5H), 8.1 m (2H), 8.5 m (2H)	**XVIIIc**	1.20 t (3H, ^3J = 7), 4.16 q (2H, ^3J = 7), 4.20 d (2H, ^3J = 6), 7.78 br.t (1H, ^3J = 6, NH)	7.55 m (6H), 7.72 m (2H), 8.38 m (2H)
Vc	1.31 d (6H, ^3J = 6), 5.70 m (1H)	7.6 m (6H), 8.1 m (2H), 8.5 m (2H)			
VIc	0.96 t (3H, ^3J = 7.5), 1.80 m (2H), 1.83 m (2H), 4.62 t (2H, ^3J = 6.5)	7.6 m (6H), 8.1 m (2H), 8.5 m (2H)	**XIXc**	3.61 m (4H), 7.22 br.t (1H, ^3J = 5, OH)	7.55 m (6H), 7.78 m (2H), 8.40 m (2H)
VIIc	3.88 m (2H), 4.69 t (2H, ^3J = 5.5), 5.0 br.t (1H, ^3J = 6, OH)	7.6 m (6H), 8.15 m (2H), 8.5 m (2H)	**XXc**	2.86 s (3H), 3.61 m (4H), 4.72 br.t (1H, ^3J = 5, OH)	7.4–7.7 m (8H), 8.40 m (2H)
VIIIc	3.55 d.d (2H, ^3J = 5.5), 4.00 m (1H), 4.59 d.d (1H, J^2 =	7.6 m (6H), 8.1 m (2H), 8.5 m (2H)	**XXIc**	2.24 s (6H), 2.75 t (2H, ^3J = 5.5), 4.71 t (2H, ^3J = 5.5)	7.6 m (6H), 8.1 m (2H), 8.5 m (2H)

glycerol molecule. The symmetric glycerol moiety in isomer **IXc** shows in the ^{1}H NMR spectrum a four-proton multiplet from two CH_2 groups, one-proton multiplet from the CH group, and two-proton triplet (^3J = 5.5 Hz) from the hydroxy groups. These data unambiguously indicate formation of the ether bond in **IXc** through the secondary β-hydroxy group of glycerol (Table 2). As follows from the signal intensities, the isomer ratio **VIIIc**:**IXc** is 10:1. Taking into account that glycerol molecule contains two primary and one secondary hydroxy groups, the rate of substitution of the 5-cyano group in **IIc** by the secondary hydroxy group is lower by a factor of 5 than the rate of replacement by primary hydroxy group.

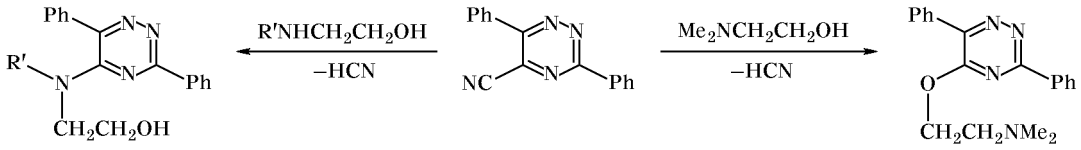
Scheme 4.



XIIc–XVIIIc **IIc** **XIc**

XII, X = NMe_2; **XIII**, X = 1-piperazinyl; **XIV**, X = 1-pyrrolidinyl; **XV**, X = piperidino; **XVI**, X = morpholino; **XVII**, X = $PhCH_2NH$; **XVIII**, X = $EtOCOCH_2NH$.

Scheme 5.



XIXc, XXc **IIc** **XXIc**

XIX, R′ = H; **XX**, R′ = Me.

Reaction of 5-cyano-1,2,4-triazine **IIc** with water as O-nucleophile in basic or acidic medium leads to formation of 3,6-diphenyl-1,2,4-triazin-5(2*H*)-one (**Xc**) in 95% yield (Scheme 1). No products of hydrolysis of the cyano group in **IIc** to amide or carboxy were detected. The structure of product **Xc** was established on the basis of the ^{1}H NMR data [10] (Table 2). Unlike aliphatic alcohols, phenols do not replace the 5-cyano group in 1,2,4-triazines, while the reactions with phenoxides resulted in tarring. No reaction with alkanethiols and benzenethiol was observed.

On the other hand, ammonia and aliphatic or cyclic amines readily replace the cyano group in **IIc** under mild conditions. By passing gaseous ammonia through a solution of **IIc** in DMF at room temperature we obtained 65% of 5-amino-3,6-diphenyl-1,2,4-triazine (**XIc**) whose properties were consistent with the proposed structure and published data [11] (Tables 1, 2). Treatment of 5-cyano-1,2,4-triazine **IIc** with dimethylamine, piperazine, pyrrolidine, piperidine, morpholine, and benzylamine gave the corresponding N-substituted 5-amino-1,2,4-triazines **XIIc**–**XVIIc** via replacement of the cyano group (Scheme 4). Amino acid esters also act as N-nucleophiles toward 5-cyano-1,2,4-triazines: The reaction of 5-cyano-3,6-diphenyl-1,2,4-triazine (**IIc**) with excess glycine ethyl ester resulted in formation of 5-ethoxycarbonylmethylamino-3,6-diphenyl-1,2,4-triazine (**XVIIIc**) in a good yield.

Amino alcohols are capable of reacting with 5-cyano-1,2,4-triazine **IIc** through both nitrogen and oxygen atoms. We have found that reactions with alcohols having a primary or secondary amino group (2-aminoethanol or 2-methylaminoethanol) yield 5-(2-hydroxyethylamino)- and 5-[2-hydroxyethyl-(methyl)amino]-3,6-diphenyl-1,2,4-triazines **XIXc** and **XXc** (Scheme 5). 2-Dimethylaminoethanol having a tertiary amino group reacts with compound **IIc** to give 5-(2-dimethylaminoethoxy)-3,6-diphenyl-1,2,4-triazine (**XXIc**) (Scheme 5). Aromatic amines failed to react with 5-cyano-3,6-diphenyl-1,2,4-triazine (**IIc**) under the same conditions.

Thus, nucleophilic substitution of hydrogen (S_N^H) by cyano group in the 1,2,4-triazine series, followed by replacement of the cyano group, provides a convenient method for preparation of a wide range of functionalized 1,2,4-triazines.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Bruker WM-250 spectrometer at 250 MHz relative to TMS as internal reference. The progress of reactions was monitored, and the purity of products was checked, by TLC on Silufol UV-254 plates using ethyl acetate as eluent; spots were visualized with UV light.

X-Ray analysis of a single crystal of compound **IIc** was performed on an Enraf–Nonius CAD-4 automatic diffractometer (λ MoK_α, graphite monochromator, ω-scanning, $2\Theta_{max}$ 54°). Monoclinic crystals with the following unit cell parameters: a = 13.595(4), b = 6.655(2), c = 14.563(7) Å; β = 104.86(3)°; Z = 4, V = 1273.6(9) Å^3; d = 1.347 g/cm^3; μ = 0.084 cm^{-1}; space group $P2_1/n$. The structure was solved by the direct method and was refined by the least-squares procedure in anisotropic approximation (isotropic for

hydrogen atoms) using SHELX-86 and SHELX-93 programs. The final divergence factors were $R = 0.051$ and $wR2 = 0.126$ for 2181 reflections with $F^2 > 3\sigma(I)$; $GOF = 1.081$.

Initial substituted 1,2,4-triazine 4-oxides **Ia**–**Ig** were synthesized by the procedure described in [12].

5-Cyano-1,2,4-triazines IIa–IIg (*general procedure***).** Acetone cyanohydrin, 1 ml (11 mmol), and triethylamine, 0.3 ml (2 mmol), were added to a suspension of 5 mmol of 1,2,4-triazine 4-oxide **Ia**–**Ig** in 50 ml of methylene chloride. The mixture was heated for 20 min under reflux and evaporated, and the residue was recrystallized from chloroform.

5-Methoxy- and 5-ethoxy-1,2,4-triazines IIIa, IIIf, IVa–IVc, and IVf. 5-Cyano-1,2,4-triazine **II**, 2 mmol, was added to a solution of 10 mg of KOH in 5 ml of methanol or ethanol, and the mixture was refluxed for 10 min. It was then diluted with water, and the precipitate was filtered off and recrystallized from methanol or ethanol.

3,6-Diphenyl-(2-propoxy)-1,2,4-triazine (Vc) and 5-butoxy-3,6-diphenyl-1,2,4-triazine (VIc) (*general procedure***).** Metallic sodium, ~50 mg, was dissolved in 4 ml of 2-propanol or 1-butanol, and 774 mg (3 mmol) of 5-cyano-3,6-diphenyl-1,2,4-triazine (**IIc**) was added. The mixture was heated for 10 min under reflux and cooled, and the precipitate was filtered off.

5-(2-Hydroxyethoxy)-3,6-diphenyl-1,2,4-triazine (VIIc). A solution of 774 mg (3 mmol) of 5-cyano-3,6-diphenyl-1,2,4-triazine (**IIc**) in a mixture of 1 ml of ethylene glycol and 2 ml of anhydrous DMF was stirred for 3 h at 80°C. The mixture was diluted with water, and the precipitate was filtered off and recrystallized from 30% ethanol.

5-(2,3-Dihydroxy-1-propoxy)-3,6-diphenyl-1,2,4-triazine (VIIIc) and 5-(1,3-dihydroxy-2-propoxy)-3,6-diphenyl-1,2,4-triazine (IXc). A solution of 774 mg (3 mmol) of 5-cyano-3,6-diphenyl-1,2,4-triazine (**IIc**) in a mixture of 1 ml of glycerol and 2 ml of anhydrous DMF was stirred for 3 h at 80°C. The mixture was diluted with water, and the precipitate was filtered off and recrystallized from 30% ethanol. An inseparable mixture of isomers **VIIIc** and **IXc** was obtained. Overall yield 820 mg (85%).

3,6-Diphenyl-1,2,4-triazin-5(2*H*)-one (Xc). *a*. 5-Cyano-3,6-diphenyl-1,2,4-triazine (**IIc**), 258 mg (1 mmol), was heated for 30 min under reflux in aqueous DMF in the presence of triethylamine. The mixture was acidified with acetic acid and diluted with water, and the precipitate was filtered off.

b. A mixture of 258 mg (1 mmol) of 5-cyano-3,6-diphenyl-1,2,4-triazine (**IIc**), 2 ml of acetic acid, and 0.5 ml of concentrated hydrochloric acid was refluxed for 10 min. It was then cooled, and the precipitate was filtered off.

5-Amino-3,6-diphenyl-1,2,4-triazine (XIc). Compound **IIc**, 258 mg (1 mmol), was dissolved in 3 ml of DMF, and dry gaseous ammonia was passed through the solution. After 30 min, the solution was

Table 3. Coordinates of non-hydrogen atoms and their temperature factors on the molecule of 5-cyano-3,6-diphenyl-1,2,4-triazine (**IIc**)

Atom	*x*	*y*	*z*	U_{iso}/U_{eq}, Å^2
N^1	0.5736 (1)	0.7800 (2)	0.5163 (1)	0.0477 (4)
N^2	0.5891 (1)	0.7817 (2)	0.6103 (1)	0.0480 (4)
N^3	0.9070 (1)	0.8141 (3)	0.4701 (1)	0.0645 (5)
N^4	0.7669 (1)	0.8227 (2)	0.6317 (1)	0.0380 (3)
C^3	0.6840 (1)	0.8082 (2)	0.6648 (1)	0.0369 (4)
C^5	0.7499 (1)	0.8180 (2)	0.5384 (1)	0.0373 (4)
C^6	0.6522 (1)	0.8010 (2)	0.4780 (1)	0.0401 (4)
C^7	0.6312 (1)	0.7969 (2)	0.3732 (1)	0.0430 (4)
C^8	0.6730 (1)	0.9390 (3)	0.3252 (1)	0.0543 (4)
C^9	0.6538 (2)	0.9325 (3)	0.2276 (1)	0.0641 (5)
C^{10}	0.5933 (1)	0.7826 (3)	0.1776 (1)	0.0647 (5)
C^{11}	0.5520 (2)	0.6419 (3)	0.2247 (1)	0.0666 (5)
C^{12}	0.5696 (1)	0.6474 (3)	0.3218 (1)	0.0544 (4)
C^{13}	0.6982 (1)	0.8156 (2)	0.7687 (1)	0.0386 (4)
C^{14}	0.6152 (1)	0.8337 (2)	0.8072 (1)	0.0461 (4)
C^{15}	0.6294 (1)	0.8402 (2)	0.9044 (1)	0.0516 (4)
C^{16}	0.7263 (1)	0.8294 (2)	0.9637 (1)	0.0483 (4)
C^{17}	0.8090 (1)	0.8112 (2)	0.9266 (1)	0.0460 (4)
C^{18}	0.7956 (1)	0.8047 (2)	0.8291 (1)	0.0415 (4)
C^{19}	0.8388 (1)	0.8194 (2)	0.5009 (1)	0.0439 (4)

Table 4. Bond lengths *d* in the molecule of 5-cyano-3,6-diphenyl-1,2,4-triazine (**IIc**)

Bond	*d*, Å	Bond	*d*, Å
N^1-N^2	1.331 (2)	N^1-C^6	1.333 (2)
N^2-C^3	1.341 (2)	N^3-C^{19}	1.129 (2)
N^4-C^5	1.319 (2)	N^4-C^3	1.338 (2)
C^3-C^{13}	1.476 (2)	C^5-C^6	1.397 (2)
C^5-C^{19}	1.449 (2)	C^6-C^7	1.479 (2)
C^7-C^8	1.382 (2)	C^7-C^{12}	1.389 (2)
C^8-C^9	1.379 (2)	C^9-C^{10}	1.376 (3)
$C^{10}-C^{11}$	1.364 (3)	$C^{11}-C^{12}$	1.372 (2)
$C^{13}-C^{14}$	1.388 (2)	$C^{13}-C^{18}$	1.391 (2)
$C^{14}-C^{15}$	1.379 (2)	$C^{15}-C^{16}$	1.380 (3)
$C^{16}-C^{17}$	1.372 (2)	$C^{17}-C^{18}$	1.386 (2)

diluted with water, and the precipitate was recrystallized from 2-propanol.

***N*-Substituted 5-amino-3,6-diphenyl-1,2,4-triazines XIIc–XVIc (*general procedure*).** 5-Cyano-3,6-diphenyl-1,2,4-triazine, 258 mg (1 mmol), was dissolved in excess amine. The mixture was kept for 24 h at 20°C and diluted with water, and the precipitate was filtered off and recrystallized from 2-propanol.

5-Benzylamino-3,6-diphenyl-1,2,4-triazine (XVIIc). A mixture of 258 mg (1 mmol) of 5-cyano-3,6-diphenyl-1,2,4-triazine (**IIc**) and 1 ml of benzylamine was heated to the boiling point and was left to stand for 2 h at room temperature. The solution was evaporated under reduced pressure, and the residue was treated with 4 ml of cold ethanol and recrystallized from ethanol.

5-(Ethoxycarbonylmethylamino)-3,6-diphenyl-1,2,4-triazine (XVIIIc). A solution of 258 mg (1 mmol) of 5-cyano-3,6-diphenyl-1,2,4-triazine (**IIc**) in 1.5 ml of a 30% solution of glycine ethyl ester in DMF was refluxed for 15 min. The mixture was diluted with 10 ml of water, the liquid phase was separated by decanting, and the residue was recrystallized from cyclohexane.

5-(2-Hydroxyethylamino)-3,6-diphenyl-1,2,4-triazine (XIXc), 5-[2-hydroxyethyl(methyl)amino]-3,6-diphenyl-1,2,4-triazine (XXc), and 5-(2-dimethylaminoethoxy)-3,6-diphenyl-1,2,4-triazine (XXIc) (*general procedure*). A solution of 258 mg (1 mmol) of 5-cyano-3,6-diphenyl-1,2,4-triazine (**IIc**) in excess aminoethanol was kept for 24 h at 20°C. It was then diluted with water, and the precipitate was filtered off.

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