Synthesis of 2-alkyl-1,2,4-benzotriazin-3(2*H*)-ones and 2-alkyl-1,4-dihydro-1,2,4-benzotriazin-3(2*H*)-ones

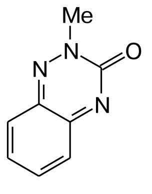
D. L. Lipilin, A. M. Churakov, Yu. A. Strelenko, and V. A. Tartakovsky*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (495) 135 5328. E-mail: lipilin@ioc.ac.ru

A preparative method for the synthesis of 2-alkyl-1,2,4-benzotriazin-3(2*H*)-ones **3** was developed. The method involves treatment with sodium cyanate of 2-alkylbenzotetrazinium tetrafluoroborates, which exist in solutions in equilibrium with *o*-(alkylazo)aryldiazonium tetrafluoroborates. Reduction of compounds **3** with zinc in acetic acid afforded 2-alkyl-1,4-dihydro-1,2,4-benzotriazin-3(2*H*)-ones.

Key words: diazonium salts, sodium cyanate, azo compounds, nitrogen-containing heterocycles, 1,2,4-benzotriazin-3-ones, nucleophilic substitution, reduction, ^{13}C NMR spectroscopy, synthetic methods.

2-Aryl-1,2,4-benzotriazin-3-ones belong to a comparatively well studied class of compounds which are attractive as antimicrobial and antiviral drugs.[1] They are usually prepared by reactions of respective *o*-amino(arylazo)benzenes with phosgene[2—4] or ethyl chloroformate.[2—5] However, 2-alkyl-1,2,4-benzotriazin-3-ones remain virtually uninvestigated. Only one compound (**A**) with such a structure has been obtained[6] in a mixture with other isomers by alkylation of the corresponding 1,2,4-benzotriazin-3-one. Note that structure **A** has been assigned to the alkylation product from its IR spectra.

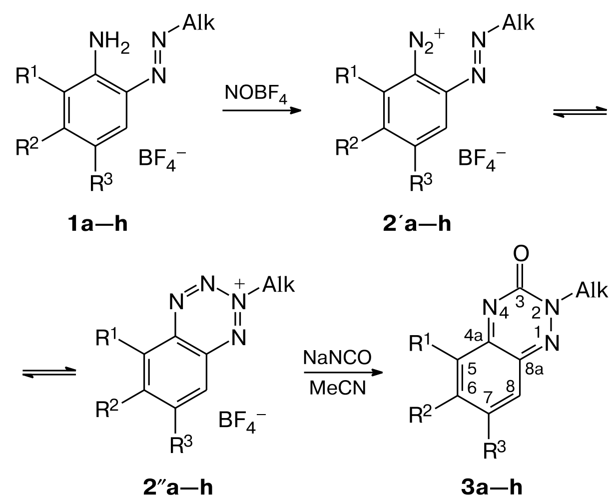


A

The goal of the present work was to develop a preparative method for the synthesis of 2-alkyl-1,2,4-benzotriazin-3(2*H*)-ones and study their reduction into 2-alkyl-1,4-dihydro-1,2,4-benzotriazin-3(2*H*)-ones. To obtain 2-alkyl-1,2,4-benzotriazin-3(2*H*)-ones, we made use of the recently[7] discovered reactions of 2-alkylbenzotetrazinium salts with nucleophiles (Hal$^-$, OAlk$^-$, OH$^-$, OAc$^-$, R$_2$NH, and CN$^-$), which occur with displacement of molecular nitrogen.

As demonstrated by us earlier,[8] 2-alkylbenzotetrazinium salts exist in solutions in equilibrium with *o*-(alkylazo)aryldiazonium salts (Scheme 1). Diazotization of the corresponding *o*-(alkylazo)anilines **1a—h** gave *o*-(alkylazo)aryldiazonium tetrafluoroborates **2´a—h**. The ratio of the open and cyclic forms in the equilibrium mixture **2´** $\rightleftharpoons$ **2″** (Table 1) was determined from the positions of signals for the Bu^t protons in the ^{1}H NMR spectra. The determination procedure has been described previously.[8]

Scheme 1



1—3	Alk	R^1	R^2	R^3	1—3	Alk	R^1	R^2	R^3
a	Bu^t	H	H	H	**e**	Bu^t	Br	H	Br
b	Bu^t	H	H	Br	**f**	Bu^t	Cl	H	Cl
c	Bu^t	H	Br	H	**g**	Bu^t	Br	Br	Br
d	Bu^t	H	H	Me	**h**	Me	Br	H	Br

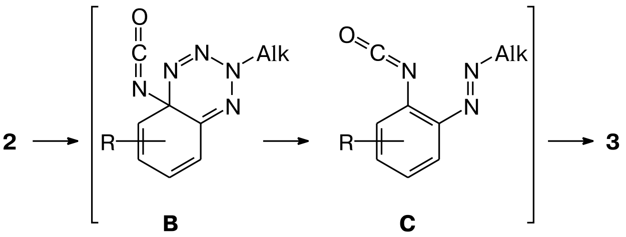
2-Alkyl-1,2,4-benzotriazin-3(2*H*)-ones. Reactions of salts **2a—h** with an excess of NaNCO (see Scheme 1) occurred in MeCN under mild conditions (5—15 min, 20 °C). The yields of benzotriazinones **3a—h** were 82—97%, regardless of the ratio of the open and cyclic forms in salts **2** (earlier,[7] this reaction has been reported only for compounds **3a,e**).

Presumably, the reaction intermediate is 1,4-dihydro-1,2,3,4-tetrazine **B**, which liberates molecular nitrogen to give isocyanate **C** undergoing cyclization into triazinone **3**

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 346—349, February, 2006.

(Scheme 2). Note that common diazonium salts do not react with sodium cyanate under these conditions, giving aryl isocyanates only in the presence of copper salts.[9]

Scheme 2



Benzotriazinones **3** can be synthesized by a "one-pot" reaction from the corresponding azoaniline **1** without isolation of salts **2**. For instance, azoaniline **1a** was converted into benzotriazinone **3a** in 86% yield.

Benzotriazinones **3a,b,g** were also obtained from the corresponding azoanilines **1** and phosgene (Scheme 3). However, this method provided good results only in the synthesis of compound **3b** (the yield was 79%). The yields of benzotriazinones **3a,g** were only 26 and 16%, respectively.

Scheme 3

$$\mathbf{1a,b,g} \xrightarrow{COCl_2} \mathbf{3a,b,g}$$

An attempted synthesis of benzotriazinone **3a** by a reaction of azoaniline **1a** with ethyl chloroformate failed, yielding a difficult-to-separate mixture of products.

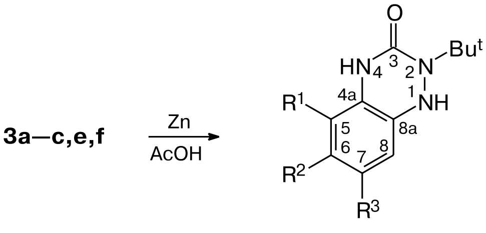
2-Alkyl-1,4-dihydro-1,2,4-benzotriazin-3(2*H*)-ones. It is known[10,11] that reduction of 1,2,4-triazin-2-ones with zinc in acetic acid gives 1,4-dihydrotriazinones. This method was suitable for reduction of benzotriazinones **3a—c,e,f** (Scheme 4). The corresponding 2-(*tert*-butyl)-1,4-dihydrobenzotriazinones **4a—e** were obtained in 75—90% yields.

Table 1. Ratio of isomers **2′** and **2″** at 297 K (see Ref. 8)

2	**2′ : 2″**	**2**	**2′ : 2″**
a	30 : 70	**e**	0 : 100
b	55 : 45	**f**	0 : 100
c	15 : 85	**g***	0 : 100
d	40 : 60	**h**	5 : 95

* The data from this study.

Scheme 4



4a—e

Compound	R^1	R^2	R^3
3a, **4a**	H	H	H
3b, **4b**	H	H	Br
3c, **4c**	H	Br	H
3e, **4d**	Br	H	Br
3f, **4e**	Cl	H	Cl

Spectroscopic studies. The cyclic structures of compounds **3** (rather than alternative open structures (see Scheme 2)) were confirmed by the absence from the IR spectra of a band of the isocyanate stretching vibrations at 2100—2300 cm^{-1}.

Complete assignment of the signals in the ^{1}H and ^{13}C NMR spectra of compounds **3** and **4** was carried out. The selective polarization transfer (SPT) technique was used to assign the signals in the ^{13}C NMR spectra. The ^{1}H and ^{13}C NMR data for 7-bromo derivatives **3b** and **4b** used as examples are given in Table 2. The downfield shift of the signals for the Bu^t protons in the ^{1}H NMR spectra

Table 2. ^{1}H and ^{13}C NMR spectra of compounds **3b** and **4b**

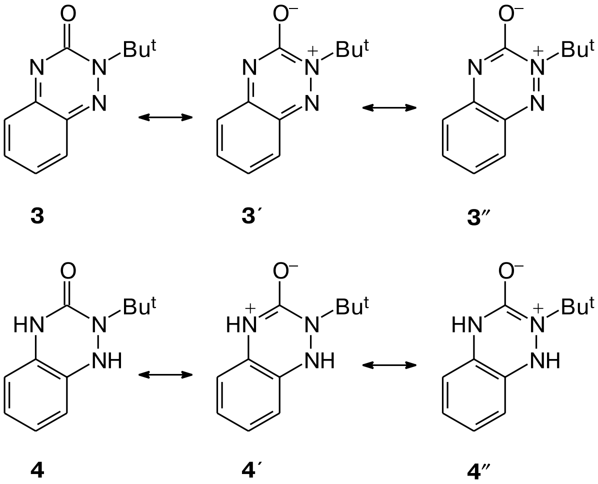
Compound	Solvent	δ_H (*J*/Hz)				δ_C*								
		Me	H(5) (d)	H(6) (dd)	H(8) (d)	$\underline{C}Me_3$	Me	C(3)	C(4a)	C(5)	C(6)	C(7)	C(8)	C(8a)
3b	Acetone-d_6	1.81	7.34 (*J* = 8.7)	8.05 (*J* = 8.7, *J* = 1.9)	7.92 (*J* = 1.9)	69.8	27.4	153.5	152.9	131.3	142.0	119.3	129.1	136.6
4b**	DMSO-d_6	1.13	6.90 (*J* = 8.3)	7.10 (*J* = 8.3, *J* = 1.6)	7.19 (*J* = 1.6)	56.4	28.4	154.5	125.6	110.3	123.1	112.3	110.9	133.9

* The assignment was performed with the use of the SPT technique.

** NH(1), δ 5.6; NH(4), δ 11.0.

of compounds **3** is evidence for their cyclic structures (for compounds **3a—h**, δ 1.77—1.81); the corresponding signals for the starting reagents **1a—h** appear at δ 1.32—1.35).[8]

It is worth noting that in partially reduced compounds **4**, the signal for the Bu^t group is shifted to a considerably higher field (δ 1.12—1.14) compared to the corresponding signal in compound **3**. Such a difference can be associated with the greater contributions from resonance structures **3**′ and **3**″ than from **4**′ and **4**″. Structures **3**′ and **3**″ favor a substantial increase in the positive charge on the N atom bound to the Bu^t group and give rise to a ring current, which results in proton deshielding.



The high positive charge on the N(2) atom also causes a downfield shift (by ~14 ppm) of the signal for the quaternary C atom of the Bu^t group in the ^{13}C NMR spectra of compounds **3** compared to compounds **4**.

Thus, we developed the general method for the synthesis of 2-alkyl-1,2,4-benzotriazin-3(2*H*)-ones and 2-alkyl-1,4-dihydro-1,2,4-benzotriazin-3(2*H*)-ones and examined their ^{1}H and ^{13}C NMR spectra.

Experimental

IR spectra were recorded on a Specord M-80 spectrophotometer. Mass spectra were recorded on a Kratos MS-30 instrument (EI, 70 eV). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer (300.13 and 75.5 MHz, respectively). The course of the reactions was monitored by TLC (Silufol UV-254); Chemapol Silica gel L 100/160 was used for column chromatography. Azoanilines **1a,b** and 2-(alkylazo)benzodiazonium tetrafluoroborates **2a—f,h** were prepared as described earlier.[8]

2,3,4-Tribromo-6-(*tert*-butylazo)aniline (1g). A solution of 1-(2-amino-3,4,5-tribromophenyl)-2-(*tert*-butyl)diazene 1-oxide (1.24 g, 2.9 mmol) in anhydrous ether (10 mL) was added at −15 °C to a stirred suspension of LiAlH$_4$ (220 mg, 5.8 mmol) in anhydrous ether (10 mL). The temperature was raised to ambient and the reaction mixture was stirred for 1 h and then poured into water. The product was extracted with ether and the extract was dried with MgSO$_4$ and concentrated *in vacuo*. The product was purified by column chromatography with CHCl$_3$ as an eluent to give yellow crystals (990 mg, 83%), m.p. 47—49 °C. Found (%): C, 28.93; H, 2.91; Br, 58.03; N, 10.13. C$_{10}$H$_{12}$Br$_3$N$_3$. Calculated (%): C, 29.02; H, 2.92; Br, 57.91; N, 10.15. IR (KBr), ν/cm^{-1}: 3310, 3460 (NH$_2$). ^{1}H NMR (acetone-d$_6$), δ: 1.34 (s, 9 H, Bu^t); 6.01 (br.s, 2 H, NH$_2$); 7.73 (s, 1 H, H(5)). MS, *m/z* (integral intensity ratio): 409, 411, 413, 415, 417 (1 : 3 : 5 : 3 : 1) [M]$^+$.

5,6,7-Tribromo-2-(*tert*-butyl)benzo-1,2,3,4-tetrazinium tetrafluoroborate (2″g). A solution of aniline **1g** (413 mg, 1 mmol) in anhydrous MeCN (5 mL) was added at −15 °C to a stirred solution of NOBF$_4$ (129 mg, 1.1 mmol) in anhydrous MeCN (5 mL). The reaction mixture was stirred under the same conditions for an additional 20 min. The solvent was removed *in vacuo* (without heating) and anhydrous ether was added. Solid salt **2″g** was filtered off, washed with ether and pentane, and dried *in vacuo* to give yellow crystals (430 mg, 84%), decomposed at 110—117 °C (without melting). Found (%): C, 23.47; H, 1.98; N, 10.89. C$_{10}$H$_{10}$BBr$_3$F$_4$N$_4$. Calculated (%): C, 23.43; H, 1.97; N, 10.93. ^{1}H NMR (acetone-d$_6$, 297 K), δ: 2.11 (s, 9 H, Bu^t); 9.57 (s, 1 H, H(5)). ^{13}C NMR (acetone-d$_6$, 297 K), δ: 29.4 (Me); 151.4 (C(5)). The chemical shifts of the signals for the protons and the C atoms were virtually the same at 273 K.

Synthesis of 2-alkyl-1,2,4-benzotriazin-3(2*H*)-ones 3a—h by reactions of salts 2a—h with sodium cyanate (general procedure). Sodium cyanate (39 mg, 0.6 mmol) was added in one portion to a stirred solution of salt **2** (0.12 mmol) in anhydrous MeCN (5 mL). The reaction mixture was stirred until the starting salt was completely consumed (5—15 min; monitoring by TLC). The precipitate of inorganic salts was filtered off and the filtrate was concentrated. The product was extracted with hot light petroleum (70—100 °C) and the extract was concentrated. Triazinones **3b—d,g,h** were purified by column chromatography with light petroleum—AcOEt (7 : 1) as an eluent.

2-(*tert*-Butyl)-1,2,4-benzotriazin-3(2*H*)-one (3a). The yield was 23 mg (95%), m.p. 110—112 °C (*cf.* Ref. 7: m.p. 110—112 °C).

7-Bromo-2-(*tert*-butyl)-1,2,4-benzotriazin-3(2*H*)-one (3b). The yield was 31 mg (92%), brown crystals, m.p. 105—107 °C. Found (%): C, 46.74; H, 4.25; Br, 28.38; N, 14.97. C$_{11}$H$_{12}$BrN$_3$O. Calculated (%): C, 46.83; H, 4.29; Br, 28.32; N, 14.89. IR (KBr), ν/cm^{-1}: 1860 (C=O). MS, *m/z* (integral intensity ratio): 281, 283 (1 : 1) [M]$^+$.

6-Bromo-2-(*tert*-butyl)-1,2,4-benzotriazin-3(2*H*)-one (3c). The yield was 30 mg (89%), brown crystals, m.p. 121—123 °C. Found (%): C, 46.73; H, 4.28; Br, 28.24; N, 14.84. C$_{11}$H$_{12}$BrN$_3$O. Calculated (%): C, 46.83; H, 4.29; Br, 28.32; N, 14.89. IR (KBr), ν/cm^{-1}: 1860 (C=O). ^{1}H NMR (acetone-d$_6$), δ: 1.78 (s, 9 H, Bu^t); 7.29 (dd, 1 H, H(7), *J* = 9.7 Hz, *J* = 1.5 Hz); 7.40 (d, 1 H, H(5), *J* = 1.5 Hz); 7.77 (d, 1 H, H(8), *J* = 9.7 Hz). ^{13}C NMR (acetone-d$_6$), δ: 27.6 (Me); 70.0 ($\underline{C}$Me$_3$); 125.3 (C(8)); 128.2 (C(7)); 130.2 (C(6)); 132.1 (C(5)); 153.7 (C(3)). MS, *m/z* (integral intensity ratio): 281, 283 (1 : 1) [M]$^+$.

2-(*tert*-Butyl)-7-methyl-1,2,4-benzotriazin-3(2*H*)-one (3d). The yield was 23 mg (90%), brown crystals, m.p. 114—116 °C. Found (%): C, 66.37; H, 6.98; N, 19.24. C$_{12}$H$_{15}$N$_3$O. Calculated (%): C, 66.34; H, 6.96; N, 19.34. IR (KBr), ν/cm^{-1}: 1840

(C=O). ^{1}H NMR (acetone-d$_6$), δ: 1.77 (s, 9 H, Bu^t); 2.40 (s, 3 H, Me); 7.24 (d, 1 H, H(5), *J* = 8.8 Hz); 7.43 (d, 1 H, H(8), *J* = 1.8 Hz); 7.58 (dd, 1 H, H(6), *J* = 8.8 Hz, *J* = 1.8 Hz). MS, *m/z*: 217 [M]$^+$.

5,7-Dibromo-2-(*tert*-butyl)-1,2,4-benzotriazin-3(2*H*)-one (3e). The yield was 43 mg (95%), m.p. 133—134 °C (*cf.* Ref. 7: m.p. 110—112 °C).

2-(*tert*-Butyl)-5,7-dichloro-1,2,4-benzotriazin-3(2*H*)-one (3f). The yield was 32 mg (97%), brown crystals, m.p. 100—102 °C. Found (%): C, 48.61; H, 4.06; Cl, 25.99; N, 15.49. $C_{11}H_{11}Cl_2N_3O$. Calculated (%): C, 48.55; H, 4.07; Cl, 26.06; N, 15.44. IR (KBr), ν/cm^{-1}: 1860 (C=O). ^{1}H NMR (acetone-d$_6$), δ: 1.80 (s, 9 H, Bu^t); 7.80 (d, 1 H, H(8), *J* = 2.0 Hz); 7.91 (d, 1 H, H(6), *J* = 2.0 Hz). ^{13}C NMR (acetone-d$_6$), δ: 27.4 (Me); 70.3 ($\underline{C}$Me$_3$); 127.2 (C(8)); 131.5 (C(7)); 136.0 (C(5)); 137.4 (C(8a)); 138.0 (C(6)); 150.2 (C(4a)); 153.0 (C(3)). MS, *m/z* (integral intensity ratio): 271, 273, 275 (4 : 2 : 1) [M]$^+$.

5,6,7-Tribromo-2-(*tert*-butyl)-1,2,4-benzotriazin-3(2*H*)-one (3g). The yield was 42 mg (82%), brown crystals, m.p. 152—155 °C. Found (%): C, 29.95; H, 2.29; Br, 54.58; N, 9.48. $C_{11}H_{10}Br_3N_3O$. Calculated (%): C, 30.03; H, 2.29; Br, 54.49; N, 9.55. IR (KBr), ν/cm^{-1}: 1870 (C=O). ^{1}H NMR (acetone-d$_6$), δ: 1.80 (s, 9 H, Bu^t); 8.12 (s, 1 H, H(8)). ^{13}C NMR (acetone-d$_6$), δ: 29.0 (Me); 70.5 ($\underline{C}$Me$_3$); 126.2 (C(8)). MS, *m/z* (integral intensity ratio): 437, 439, 441, 443 (1 : 3 : 3 : 1) [M]$^+$.

5,7-Dibromo-2-methyl-1,2,4-benzotriazin-3(2*H*)-one (3h). The yield was 32 mg (84%), brown crystals, m.p. 102—105 °C. Found (%): C, 29.85; H, 1.72; Br, 49.81; N, 13.55. $C_8H_5Br_2N_3O$. Calculated (%): C, 30.13; H, 1.58; Br, 50.10; N, 13.17. IR (KBr), ν/cm^{-1}: 1880 (C=O). ^{1}H NMR (acetone-d$_6$), δ: 4.09 (s, 3 H, Me); 7.94 (d, 1 H, H(8), *J* = 2.2 Hz); 8.16 (d, 1 H, H(6), *J* = 2.2 Hz). MS, *m/z* (integral intensity ratio): 317, 319, 321 (1 : 2 : 1) [M]$^+$.

Synthesis of 2-(*tert*-butyl)-1,2,4-benzotriazin-3(2*H*)-one (3a) from *o*-(*tert*-butylazo)aniline (1a). A solution of aniline **1a** (177 mg, 1 mmol) in anhydrous MeCN (5 mL) was added at −15 °C to a stirred suspension of NOBF$_4$ (129 mg, 1.1 mmol) in anhydrous MeCN (5 mL). The reaction mixture was stirred under the same conditions for 20 min. Then NaNCO (325 mg, 5 mmol) was added, the temperature was raised to ambient, and stirring was continued for 15 min. The precipitate of inorganic salts was filtered off and the filtrate was concentrated. The product was extracted from the residue with hot (70—100 °C) light petroleum and the extract was concentrated. Column chromatography with light petroleum—AcOEt (7 : 1) as an eluent gave compound **3a** (175 mg, 86%), which was identical with that obtained earlier.

Synthesis of 2-alkyl-1,2,4-benzotriazin-3(2*H*)-ones 3a,b,g by reactions of *o*-azoanilines 1a,b,g with phosgene (general procedure). Phosgene was slowly passed through a stirred solution of azoaniline **1** (1.8 mmol) in CHCl$_3$ (27 mL) until the starting compound was completely consumed (15—45 min, monitoring by TLC). The solvent was removed *in vacuo* and the residue was purified by column chromatography with CHCl$_3$ as an eluent.

2-(*tert*-Butyl)-1,2,4-benzotriazin-3(2*H*)-one (3a). The yield was 95 mg (26%); the product was identical with that obtained earlier.

7-Bromo-2-(*tert*-butyl)-1,2,4-benzotriazin-3(2*H*)-one (3b). The yield was 400 mg (79%); the product was identical with that obtained earlier.

5,6,7-Tribromo-2-(*tert*-butyl)-1,2,4-benzotriazin-3(2*H*)-one (3g). The yield was 127 mg (16%); the product was identical with that obtained earlier.

Synthesis of 2-alkyl-1,4-dihydro-1,2,4-benzotriazin-3(2*H*)-ones 4a—e by reduction of benzotriazin-3-ones 3a—c,e,f with zinc in acetic acid (general procedure). Pulverized zinc (96 mg) was added to a solution of benzotriazin-3-one **3** (0.79 mmol) in a mixture of AcOH (19.2 mL) and EtOH (3.2 mL). The reaction mixture was refluxed for 2 h and filtered hot to separate inorganic salts. The filtrate was concentrated *in vacuo* by ~90%. Cold water (10 mL) was added to the residue and the product that formed was filtered off, thoroughly washed with water, and dried in air.

2-(*tert*-Butyl)-1,4-dihydro-1,2,4-benzotriazin-3(2*H*)-one (4a). The yield was 134 mg (83%), gray crystals, m.p. 193—194.5 °C. Found (%): C, 64.46; H, 7.36; N, 20.42. $C_{11}H_{15}N_3O$. Calculated (%): C, 64.37; H, 7.37; N, 20.47. IR (KBr), ν/cm^{-1}: 1680 (C=O); 2890, 3180, 3240 (NH). ^{1}H NMR (DMSO-d$_6$), δ: 1.14 (s, 9 H, Bu^t); 5.44 (s, 1 H, N(1)H); 6.95 (m, 3 H, H(5), H(6), H(7)); 7.08 (dd, 1 H, H(8), *J* = 6.7 Hz, *J* = 2.0 Hz); 10.78 (s, 1 H, N(4)H). ^{13}C NMR (DMSO-d$_6$), δ: 28.4 (Me); 56.3 ($\underline{C}$Me$_3$); 108.5 (C(5) or C(8)); 108.6 (C(5) or C(8)); 120.4 (C(6) or C(7)); 120.5 (C(6) or C(7)); 126.3 (C(4a)); 132.4 (C(8a)); 154.6 (C(3)). MS, *m/z*: 205 [M]$^+$.

7-Bromo-2-(*tert*-butyl)-1,4-dihydro-1,2,4-benzotriazin-3(2*H*)-one (4b). The yield was 197 mg (88%), light gray crystals, m.p. 227—229 °C. Found (%): C, 46.42; H, 4.97; Br, 28.20; N, 15.03. $C_{11}H_{14}BrN_3O$. Calculated (%): C, 46.50; H, 4.97; Br, 28.12; N, 14.79. IR (KBr), ν/cm^{-1}: 1690 (C=O); 2890, 3200, 3240 (NH). MS, *m/z* (integral intensity ratio): 283, 285 (1 : 1) [M]$^+$.

6-Bromo-2-(*tert*-butyl)-1,4-dihydro-1,2,4-benzotriazin-3(2*H*)-one (4c). The yield was 197 mg (90%), light gray crystals, m.p. 202—205 °C. Found (%): C, 46.35; H, 5.12; Br, 27.89; N, 14.55. $C_{11}H_{14}BrN_3O$. Calculated (%): C, 46.50; H, 4.97; Br, 28.12; N, 14.79. IR (KBr), ν/cm^{-1}: 1690 (C=O); 2900, 3200, 3250 (NH). ^{1}H NMR (DMSO-d$_6$), δ: 1.14 (s, 9 H, Bu^t); 5.52 (s, 1 H, N(1)H)); 6.91 (dd, 1 H, H(7), *J* = 8.9 Hz, *J* = 1.8 Hz); 7.03 (d, 1 H, H(5), *J* = 1.8 Hz); 7.22 (d, 1 H, H(8), *J* = 8.9 Hz); 11.1 (s, 1 H, N(4)H). MS, *m/z* (integral intensity ratio): 283, 285 (1 : 1) [M]$^+$.

5,7-Dibromo-2-(*tert*-butyl)-1,4-dihydro-1,2,4-benzotriazin-3(2*H*)-one (4d). The yield was 215 mg (75%), light gray crystals, m.p. 236—238 °C. Found (%): C, 36.46; H, 3.60; Br, 43.94; N, 11.62. $C_{11}H_{13}Br_2N_3O$. Calculated (%): C, 36.39; H, 3.61; Br, 44.02; N, 11.57. IR (KBr), ν/cm^{-1}: 1690 (C=O); 2880, 3200, 3220 (NH). ^{1}H NMR (DMSO-d$_6$), δ: 1.12 (s, 9 H, Bu^t); 5.56 (s, 1 H, N(1)H); 7.12 (d, 1 H, H(8), *J* = 2.0 Hz); 7.25 (d, 1 H, H(6), *J* = 2.0 Hz); 11.2 (s, 1 H, N(4)H). ^{13}C NMR (DMSO-d$_6$), δ: 28.4 (Me); 56.2 ($\underline{C}$Me$_3$); 110.1 (C(8)); 125.1 (C(6)); 154.4 (C(3)). MS, *m/z* (integral intensity ratio): 361, 363, 365 (1 : 2 : 1) [M]$^+$.

2-(*tert*-Butyl)-5,7-dichloro-1,4-dihydro-1,2,4-benzotriazin-3(2*H*)-one (4e). The yield was 184 mg (85%), light gray crystals, m.p. 189—191 °C. Found (%): C, 48.19; H, 4.78; Cl, 25.86; N, 15.33. $C_{11}H_{13}Cl_2N_3O$. Calculated (%): C, 48.43; H, 4.92; Cl, 25.67; N, 15.21. IR (KBr), ν/cm^{-1}: 1700 (C=O); 2880, 3210, 3250 (NH). ^{1}H NMR (DMSO-d$_6$), δ: 1.12 (s, 9 H, Bu^t); 5.55 (s, 1 H, N(1)H); 6.80 (d, 1 H, H(8), *J* = 2.1 Hz); 6.92 (d, 1 H, H(6), *J* = 2.1 Hz); 10.9 (s, 1 H, N(4)H). MS, *m/z* (integral intensity ratio): 273, 275, 277 (4 : 2 : 1) [M]$^+$.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 04-03-32432).

References

1. J. Slouka and V. Bekarek, *Coll. Czech. Chem. Commun.*, 1980, **45**, 1379.
2. M. Busch, *Ber.*, 1899, **32**, 2959.
3. P. Pierron, *Ann. Chim. (Paris)*, 1908, **15**, 213.
4. P. Pierron, *Ann. Chim. (Paris)*, 1908, **15**, 252.
5. J. Slouka, *Pharmazie*, 1988, **43**, 864.
6. L. Ergener, *Rev. Faculte Sci. Univ. Istambul*, 1950, **15A**, 91.
7. D. L. Lipilin, O. Yu. Smirnov, A. M. Churakov, Yu. A. Strelenko, A. Yu. Tyurin, S. L. Ioffe, and V. A. Tartakovsky, *Eur. J. Org. Chem.*, 2004, 4794.
8. D. L. Lipilin, P. A. Belyakov, Yu. A. Strelenko, A. M. Churakov, O. Yu. Smirnov, S. L. Ioffe, and V. A. Tartakovsky, *Eur. J. Org. Chem.*, 2002, 3821.
9. H. Zollinger, *DiazoChemistry I: Aromatic and Heteroaromatic Compounds*, VCH, Weinheim, 1994.
10. M. M. M. Sallam, Y. A. Ibrahim, and S. A.-L. Abdel-Hady, *Helv. Chim. Acta*, 1976, **59**, 1093.
11. A. Mustafa, W. Asker, A. K. Mansouz, H. A. A. Zaher, and A. R. Eloui, *J. Org. Chem.*, 1963, **28**, 3519.

Received July 14, 2005;
in revised form October 20, 2005