FULL PAPER

One-Pot Synthesis of 3-Substituted 3,4-Dihydro-1,2,3-benzotriazine Derivatives Based on the Reaction of *o*-Bromobenzyl Azides with Butyllithium

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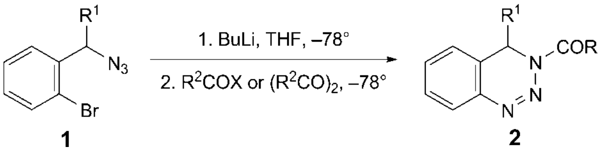
An efficient one-pot procedure for the preparation of 3-substituted 3,4-dihydro-1,2,3-benzotriazines **2**, **3**, and **4** from *o*-bromobenzyl azides **1** is described. The reaction of these azides with BuLi in THF at −78° generates *o*-lithiobenzyl azides *via* the Br/Li exchange. These lithium compounds immediately undergo intramolecular cyclization to give the corresponding (dihydro-1,2,3-benzotriazinyl)lithium intermediates, which are trapped with a variety of acylating agents or BnBr at N(3) exclusively to provide the desired products in moderate to good yields.

Introduction. – In recent years, much attention has been paid to compounds with the 1,2,3-benzotriazine structure because of their biological activities [1]. However, to date, there have been only a few efficient procedures for the practical synthesis of 3-substituted 3,4-dihydro-1,2,3-benzotriazines [2 – 4]. For example, *Igeta et al.* have reported the formation of 3,4-dihydro-1,2,3-benzotriazine derivatives by the reaction of 1,2,3-benzotriazine 3-oxides with PhMgBr [2]. Recently, the synthesis of 3-acyl-4-alkyl-3,4-dihydro-1,2,3-benzotriazines by cyclization of acylated *o*-triazenylbenzylamines was described by *Reingruber et al.* [4]. As part of our study on the preparation of benzene-fused heterocyclic compounds utilizing *o*-functionalized benzyl azides [5], we now wish to report the treatment of *o*-bromobenzyl azides **1** with BuLi followed by addition of acylating agents affording 3-acyl-3,4-dihydro-1,2,3-benzotriazines **2** and **3** in a one-pot procedure. We also demonstrate that the use of a haloalkane, such as BnBr, makes possible to provide 3-benzyl-3,4-dihydro-1,2,3-benzotriazines **4**. This is a rare example of the addition of organometals to the azide terminal nitrogen, though the formation of 3-alkyl-3,4-dihydro-1,2,3-benzotriazin-4-imines by the reaction of 2-azidobenzonitrile with *Grignard* reagents has been described [6].

Results and Discussion. – Our one-pot synthesis of **2** from **1** was conducted according to the procedure illustrated in *Scheme 1.* Thus, compounds **1**, readily prepared from the respective *o*-bromobenzyl bromides, were treated with BuLi in THF at −78°. Acylating agents were then added at the same temperature to result in the exclusive isolation of the 3-acylated products **2** after aqueous workup and the subsequent purification by column chromatography on SiO_2. The results are compiled in the *Table*, which indicate the present reaction is general for a range of acylating agents and that the yields are generally fair, whereas the yield of the product using di-*tert*-butyl dicarbonate is somewhat lower than those using the other acylating agents, as can be seen from *Entry 5*. The substituents at the 4-position of the products give little influence on the yields. The 3-acyalted 3,4-dihydro-1,2,3-benzotriazine structure of **2** was determined on the basis of their spectral data (IR, ^{1}H- and ^{13}C-NMR, and MS) and elemental analyses. Especially, the IR and ^{1}H-NMR spectral data of 1-(4-phenyl-1,2,3-benzotriazin-3(4*H*)-yl)-ethanone (**2l**) are identical to those reported previously by *Golik* and *Taub* [3]. These authors synthesized this compound by the reaction of diazotized *N*-acetyl-2-aminobenzhydrylamines with Na_2CO_3.

Scheme 1



Pentanedioyl chloride proved to be usable in the present reaction. Thus, the reaction of **1a** with BuLi under the conditions as described above was followed by treatment with pentanedioyl dichloride (2 : 2 : 1 molar ratio) to result in the formation of bis(3,4-dihydro-1,2,3-benzotriazin-3-yl)pentane-1,5-dione (**3**) in a reasonable yield as outlined in *Scheme 2*.

Introduction of an alkyl group at the 3-position of 3,4-dihydro-1,2,3-benzotriazine was subsequently carried out, as illustrated in *Scheme 3*. After the treatment of **1** with BuLi as described above for the preparation of **2**, BnBr was added. However, benzylation proceeded slowly even at room temperature, and the corresponding desired products **4** were isolated in low-to-moderate yields after column chromatography on SiO_2 from rather complicated mixtures

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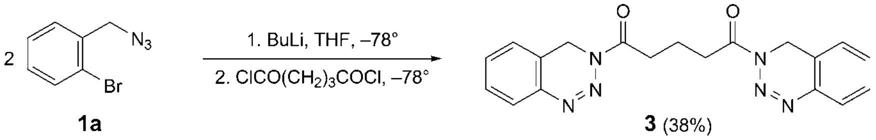
Table. *Preparation of 3-Acyl-3,4-dihydro-1,2,3-benzotriazines* **2**

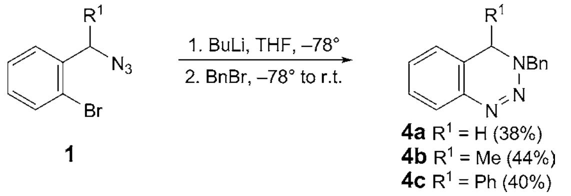
Entry	**1**	R^2COX or $(R^2CO)_2O$	**2**	Yield [%][a])
1	**1a** ($R^1 = H$)	BzCl	**2a**	83
2	**1a**	2-Cl–C_6H_4COCl	**2b**	57
3	**1a**	EtOCOCl	**2c**	72
4	**1a**	Ac_2O	**2d**	62
5	**1a**	$(t\text{-}BuOCO)_2O$	**2e**	41
6	**1b** ($R^1 = Me$)	BzCl	**2f**	74
7	**1b**	2-Me–C_6H_4COCl	**2g**	71
8	**1b**	4-Cl–C_6H_4COCl	**2h**	64
9	**1b**	EtOCOCl	**2i**	57
10	**1b**	Ac_2O	**2j**	56
11	**1c** ($R^1 = Ph$)	EtOCOCl	**2k**	62
12	**1c**	Ac_2O	**2l** [3]	54

[a]) Yields of isolated products.

Scheme 2



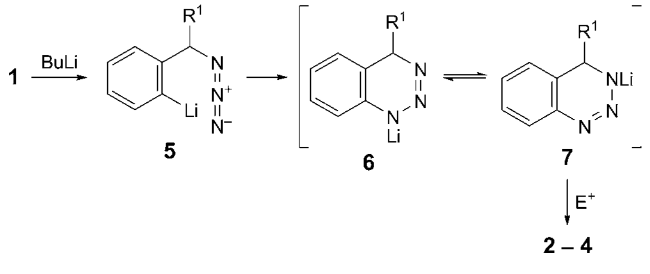
Scheme 3



of products. The structure of **4** was elucidated by NOESY analyses of **4b**, which revealed an interaction between the 4-Me H-atoms and one of the benzyl H-atoms.

A probable pathway from **1** to **2**–**4** is illustrated in *Scheme 4*. Thus, *o*-lithiobenzyl azides **5** are generated by the Br/Li exchange between **1** and BuLi. These undergo immediate cyclization by intramolecular attack on the terminal N of the azide moiety to provide tautomeric benzotriazinide anion intermediates **6** and **7**, which are trapped exclusively at the N(3) (*i.e.* **7**) by adding acylating agents or BnBr to give rise to 3-acylated or benzylated products **2**–**4**. This regioselectivity possibly arises from the difference of the nucleophilic reactivity between the N(3) and N(1).

Scheme 4



In conclusion, we have succeeded in the development of a convenient one-pot method for the preparation of 3-substituted 3,4-dihydro-1,2,3-benzotriazines from *o*-bromobenzyl azides using BuLi and acylating agents or BnBr. The present method may be of use in organic synthesis due to the ready availability of the starting materials, and may provide interesting pharmacophores. Further work on the preparation of related heterocycles by utilizing *o*-bromobenzyl azides is currently under way in our laboratory.

Experimental Part

General. All org. solvents used in this study were dried over appropriate drying agents and distilled prior to use. TLC: *Merck* silica gel *60 PF_{254}*. Column chromatography (CC): *Wako Gel C-200E.* M.p.: *Laboratory Devices MEL-TEMP II* melting-point apparatus; uncorrected. IR Spectra: *Perkin–Elmer Spectrum65* FT-IR spectrophotometer; $\tilde{\nu}$ in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *JEOL ECP500* FT NMR spectrometer (at 500 and 125 MHz, resp.); in $CDCl_3$; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. HR-MS: *Thermo Scientific Exactive* (DART or ESI, pos.) or *JEOL JMS-T100GCV* (EI, TOF; 70 eV) spectrometer; in *m*/*z*. Elemental analyses: *Elementar Vario EL II* instrument.

1-Bromo-2-(1-bromoethyl)benzene [7], *1-bromo-2-[chloro(phenyl)methyl]benzene* [8], and *1-azidomethyl-2-bromobenzene* (**1a**) [9] were prepared according to the appropriate reported procedures. BuLi was supplied by *Asia Lithium Corporation.* All other chemicals used in this study were commercially available.

1-(1-Azidoethyl)-2-bromobenzene (**1b**) [10]. *Representative Procedure.* A soln. of 1-bromo-2-(1-bromoethyl)benzene (2.4 g, 9.1 mmol) in DMSO (20 ml) containing NaN_3 (0.65 g, 10 mmol) was stirred overnight at r.t. H_2O (50 ml) was added and the mixture was extracted with AcOEt (3 × 25 ml). The combined extracts were washed with H_2O (3 × 25 ml) and brine (20 ml), dried (Na_2SO_4), and concentrated by evaporation. The residue was purified by CC (SiO_2) to afford **1b** (1.8 g, 86%). Colorless liquid. R_f (CH_2Cl_2/hexane 1:40) 0.36. IR (neat): 2094. ^1H-NMR: 1.51 (*d*, *J* = 6.9, 3 H); 5.11 (*q*, *J* = 6.9, 1 H); 7.17 (*td*,

$J = 7.4$, 1.7, 1 H); 7.36 (*ddd*, $J = 8.0$, 7.4, 1.7, 1 H); 7.47 (*dd*, $J = 7.4$, 1.7, 1 H); 7.57 (*dd*, $J = 8.0$, 1.7, 1 H).

1-[Azido(phenyl)methyl]-2-bromobenzene (**1c**). Colorless oil. R_f (CH_2Cl_2/hexane 1 : 5) 0.36. IR (neat): 2100. ^{1}H-NMR: 6.16 (*s*, 1 H); 7.19 (*ddd*, $J = 8.0$, 7.4, 1.7, 1 H); 7.30 – 7.38 (*m*, 6 H); 7.49 (*dd*, $J = 8.0$, 1.7, 1 H); 7.57 (*dd*, $J = 8.0$, 1.1, 1 H). Anal. calc. for $C_{13}H_{10}BrN_3$ (288.14): C 54.19, H 3.50, N 14.58; found: C 54.07, H 3.68, N 14.28.

*1,2,3-Benzotriazin-3(4*H*)-yl(phenyl)methanone* (**2a**). *Representative Procedure.* To a stirred soln. of **1a** (0.21 g, 1.0 mmol) in THF at – 78° was added BuLi (1.6M in hexane, 1.0 mmol) dropwise. After 5 min, a soln. of BzCl (0.14 g, 1.0 mmol) in THF (2 ml) was added slowly. H_2O (20 ml) was then added, and the mixture was warmed to r.t. and extracted with AcOEt (3 × 10 ml). The combined extracts were washed with aq. 10% NaOH, H_2O, and brine (10 ml each), then dried (Na_2SO_4), and finally concentrated by evaporation. The residual solid was recrystallized from hexane/CH_2Cl_2 to give **2a** (0.20 g, 83%). Pale-yellow solid. M.p. 103 – 105°. IR (KBr): 1672. ^{1}H-NMR: 4.92 (*s*, 2 H); 7.18 (*dd*, $J = 6.3$, 2.3, 1 H); 7.44 – 7.51 (*m*, 4 H); 7.54 (*t*, $J = 7.4$, 1 H); 7.74 (*dd*, $J = 6.9$, 2.3, 1 H); 7.78 (*dd*, $J = 6.9$, 1.7, 2 H). ^{13}C-NMR: 38.88; 119.26; 126.28; 127.79; 127.91; 129.22; 130.37; 131.69; 132.24; 133.03; 136.29; 171.94. HR-ESI-MS: 238.0973 ($[M+H]^+$, $C_{14}H_{12}N_3O^+$; calc. 238.0980). Anal. calc. for $C_{14}H_{11}N_3O$ (237.26): C 70.87, H 4.67, N 17.71; found: C 70.81, H 4.70, N 17.64.

*1,2,3-Benzotriazin-3(4*H*)-yl(2-chlorophenyl)methanone* (**2b**). White solid. M.p. 101 – 102° (hexane/CH_2Cl_2). IR (KBr): 1687. ^{1}H-NMR: 5.00 (*s*, 2 H); 7.17 (*d*, $J = 7.4$, 1 H); 7.34 – 7.50 (*m*, 6 H); 7.70 (*d*, $J = 7.4$, 1 H). ^{13}C-NMR: 38.59; 118.34; 126.39; 126.62; 128.39; 128.84; 129.31; 129.48; 130.95; 131.33; 132.47; 134.67; 135.76; 170.69. HR-ESI-MS: 272.0585 ($[M+H]^+$, $C_{14}H_{11}ClN_3O^+$; calc. 272.0590). Anal. calc. for $C_{14}H_{10}ClN_3O$ (271.70): C 61.89, H 3.71, N 15.47; found: C 61.66, H 3.88, N 15.43.

*Ethyl 1,2,3-Benzotriazine-3(4*H*)-carboxylate* (**2c**). Pale-yellow solid. M.p. 93 – 95° (hexane/CH_2Cl_2). IR (KBr): 1718. ^{1}H-NMR: 1.43 (*t*, $J = 7.4$, 3 H); 4.46 (*q*, $J = 7.4$, 2 H); 4.76 (*s*, 2 H); 7.07 (*dd*, $J = 4.6$, 3.4, 1 H); 7.41 – 7.44 (*m*, 2 H); 7.70 (*dd*, $J = 4.6$, 4.0, 1 H). ^{13}C-NMR: 14.43; 39.85; 63.66; 119.04; 125.90; 127.81; 129.18; 132.03; 136.04; 154.29. HR-ESI-MS: 206.0923 ($[M+H]^+$, $C_{10}H_{12}N_3O_2^+$; calc. 206.0929). Anal. calc. for $C_{10}H_{11}N_3O_2$ (205.21): C 58.53, H 5.40, N 20.48; found: C 58.29, H 5.43, N 20.27.

*1-(1,2,3-Benzotriazin-3(4*H*)-yl)ethanone* (**2d**). White solid. M.p. 119 – 121° (hexane/CH_2Cl_2). IR (KBr): 1693. ^{1}H-NMR: 2.59 (*s*, 3 H); 4.80 (*s*, 2 H); 7.09 (*dd*, $J = 6.3$, 2.9, 1 H); 7.41 – 7.45 (*m*, 2 H); 7,70 (*dd*, $J = 6.3$, 2.9, 1 H). ^{13}C-NMR: 21.58; 38.18; 118.63; 126.30; 127.98; 129.17; 132.11; 135.81; 173.71. HR-ESI-MS: 176.0816 ($[M+H]^+$, $C_9H_{10}N_3O^+$; calc. 176.0824). Anal. calc. for $C_9H_9N_3O$ (175.19): C 61.70, H 5.18, N 23.99; found: C 61.70, H 5.21, N 23.81.

tert-*Butyl 1,2,3-Benzotriazine-3(4*H*)-carboxylate* (**2e**). Pale-yellow solid. M.p. 83 – 84° (hexane/CH_2Cl_2). IR (KBr): 1714: ^{1}H-NMR: 1.62 (*s*, 9 H); 4.71 (*s*, 2 H); 7.06 (*dd*, $J = 4.6$, 4.0, 1 H); 7.40 (*dd*, $J = 7.4$, 4.0, 1 H); 7.42 (*dd*, $J = 7.4$, 3.4, 1 H); 7.67 (*dd*, $J = 5.1$, 3.4, 1 H). ^{13}C-NMR: 28.14; 39.68; 83.66; 119.38; 125.87; 127.49; 129.09; 131.74; 136.30; 152.85. HR-ESI-MS: 234.1237 ($[M+H]^+$, $C_{12}H_{16}N_3O_2^+$; calc. 234.1242). Anal. calc. for $C_{12}H_{15}N_3O_2$ (233.27): C 61.79, H 6.48, N 18.01; found: C 61.70, H 6.62, N 17.98.

*(4-Methyl-1,2,3-benzotriazin-3(4*H*)-yl)(phenyl)methanone* (**2f**). Beige solid. M.p. 95 – 97° (hexane/CH_2Cl_2). IR (KBr): 1679, 1602. ^{1}H-NMR: 1.40 (*d*, $J = 6.3$, 3 H); 5.64 (*q*, $J = 6.3$, 1 H); 7.17 (*d*, $J = 6.9$, 1 H); 7.44 (*t*, $J = 7.4$, 2 H); 7.47 – 7.53 (*m*, 3 H); 7.72 (*d*, $J = 7.4$, 2 H); 7.76 (*dd*, $J = 7.4$, 1.1, 1 H). ^{13}C-NMR: 21.90; 45.15; 125.53 (2 overlapped Cs); 127.24; 127.85; 128.96; 130.29; 131.56; 132.38; 133.45; 136.43; 171.42. HR-ESI-MS: 252.1132 ($[M+H]^+$, $C_{15}H_{14}N_3O^+$; calc. 252.1137). Anal. calc. for $C_{15}H_{13}N_3O$ (251.28): C 71.70, H 5.21, N 16.72; found: C 71.44, H 5.32, N 16.51.

*(4-Methyl-1,2,3-benzotriazin-3(4*H*)-yl)(2-methylphenyl)methanone* (**2g**). Pale-yellow solid. M.p. 78 – 81° (hexane/CH_2Cl_2). IR (KBr): 1680. ^{1}H-NMR: 1.43 (*d*, $J = 6.9$, 3 H); 2.33 (*s*, 3 H); 5.74 (*q*, $J = 6.9$, 1 H); 7.18 (*dd*, $J = 7.4$, 1.1, 1 H); 7.23 (*t*, $J = 7.4$, 1 H); 7.24 (*d*, $J = 7.4$, 1 H); 7.29 (*d*, $J = 8.0$, 1 H); 7.34 (*ddd*, $J = 8.0$, 7.4, 1.1, 1 H); 7.46 (*td*, $J = 7.4$, 1.1, 1 H); 7.51 (*td*, $J = 7.4$, 1.1, 1 H); 7.72 (*dd*, $J = 7.4$, 1.1, 1 H). ^{13}C-NMR: 19.47; 22.43; 44.60; 125.03; 125.37; 125.68; 127.56; 127.62; 129.02; 129.81; 130.25; 132.45; 134.80; 135.43; 136.18; 173.06. HR-ESI-MS: 266.1288 ($[M+H]^+$, $C_{16}H_{16}N_3O^+$; calc. 266.1293). Anal. calc. for $C_{16}H_{15}N_3O$ (265.31): C 72.43, H 5.70, N 15.84; found: C 72.30, H 5.82, N 15.90.

*(4-Chlorophenyl)(4-methyl-1,2,3-benzotriazin-3(4*H*)-yl)methanone* (**2h**). White solid. M.p. 72 – 74° (hexane/CH_2Cl_2). IR (KBr): 1673. ^{1}H-NMR: 1.39 (*d*, $J = 6.9$, 3 H); 5.62 (*q*, $J = 6.9$, 1 H); 7.18 (*dd*, $J = 7.4$, 1.7, 1 H); 7.42 (*d*, $J = 8.6$, 2 H); 7.48 – 7.54 (*m*, 2 H); 7.68 (*d*, $J = 8.6$, 2 H); 7.77 (*dd*, $J = 7.4$, 1.1, 1 H). ^{13}C-NMR: 21.93; 45.26; 125.44; 125.56; 127.38; 128.19; 129.06; 131.78; 131.83; 132.56; 136.38; 137.93; 170.29. HR-ESI-MS: 286.0742 ($[M+H]^+$, $C_{15}H_{13}ClN_3O^+$; calc. 286.0747). Anal. calc. for $C_{15}H_{12}ClN_3O$ (285.73): C 63.05, H 4.23, N 14.71; found: C 62.97, H 4.18, N 14.65.

*Ethyl 4-Methyl-1,2,3-benzotriazine-3(4*H*)-carboxylate* (**2i**). Yellow oil. R_f (AcOEt/hexane 1 : 7) 0.27. IR (neat): 1723. ^{1}H-NMR: 1.31 (*d*, $J = 6.3$, 3 H); 1.43 (*t*, $J = 7.4$, 3 H); 4.41 – 4.52 (*m*, 2 H); 5.34 (*q*, $J = 6.3$, 1 H); 7.09 (*dd*, $J = 6.9$, 1.7, 1 H); 7.42 – 7.48 (*m*, 2 H); 7.73 (*d*, $J = 6.9$, 2.2, 1 H). ^{13}C-NMR: 14.41; 22.25; 46.34; 63.55; 125.23; 125.28; 127.29; 129.00; 132.13; 136.11; 153.85. HR-ESI-MS: 220.1079 ($[M+H]^+$, $C_{11}H_{14}N_3O_2^+$; calc. 220.1086). Anal. calc. for $C_{11}H_{13}N_3O_2$ (219.24): C 60.26, H 5.98, N 19.17; found: C 60.26, H 6.04, N 19.06.

*1-(4-Methyl-1,2,3-benzotriazin-3(4*H*)-yl)ethanone* (**2j**). Beige solid. M.p. 52 – 53° (hexane/CH_2Cl_2). IR (KBr): 1700. ^{1}H-NMR: 1.28 (*d*, $J = 6.9$, 3 H); 2.58 (*s*, 3 H); 5.57 (*q*, $J = 6.9$, 1 H); 7.10 (*dd*, $J = 6.3$, 1.7, 1 H); 7.43 – 7.48 (*m*, 2 H); 7.73 (*dd*, $J = 6.9$, 2.3, 1 H). ^{13}C-NMR: 21.86; 22.66; 44.05; 124.98; 125.64; 127.31; 128.88; 132.21; 136.15; 173.19. HR-ESI-MS: 190.0975 ($[M+H]^+$, $C_{10}H_{12}N_3O^+$; calc. 190.0980). Anal. calc. for $C_{10}H_{11}N_3O$ (189.21): C 63.48, H 5.86, N 22.21; found: C 63.28, H 5.88, N 22.08.

*Ethyl 4-Phenyl-1,2,3-benzotriazine-3(4*H*)-carboxylate* (**2k**). White solid. M.p. 75 – 77° (hexane/CH_2Cl_2). IR (KBr): 1725. ^{1}H-NMR: 1.37 (*t*, $J = 6.9$, 3 H); 4.32 – 4.46 (*m*, 2 H); 6.30 (*s*, 1 H); 7.09 (*dd*, $J = 6.9$, 1.7, 1 H); 7.18 (*d*, $J = 6.9$, 2 H); 7.24 – 7.29 (*m*, 3 H); 7.41 – 7.47 (*m*, 2 H); 7.80 (*dd*, $J = 7.4$, 1.7, 1 H). ^{13}C-NMR: 14.32; 53.73; 63.73; 122.83; 126.59; 126.68; 127.79; 128.34; 128.84; 129.17; 132.41; 135.38; 141.34; 153.86. HR-MS (DART): 282.1233 ($[M+H]^+$, $C_{16}H_{16}N_3O_2^+$; calc. 282.1242). Anal. calc. for $C_{16}H_{15}N_3O_2$ (281.31): C 68.31, H 5.37, N 14.94; found: C 68.21, H 5.41, N 14.76.

*1-(4-Phenyl-1,2,3-benzotriazin-3(4*H*)-yl)ethanone* (**2l**). White solid. M.p. 95 – 96° (hexane/CH_2Cl_2) ([3] 96 – 97°). The spectral (IR and ^{1}H-NMR) data for this product were identical to those reported in [3].

*1,5-Bis(1,2,3-benzotriazin-3(4*H*)-yl)pentane-1,5-dione* (**3**). Beige solid. M.p. 147 – 149° (hexane/$CHCl_3$). IR (KBr): 1697. ^{1}H-NMR: 2.24 (*quint*, $J = 7.4$, 2 H); 3.13 (*t*, $J = 7.4$, 4 H); 4.79 (*s*, 4 H); 7.09 (*dd*, $J = 8.0$, 1.7, 2 H); 7.41 – 7.43 (*m*, 4 H); 7.67 (*dd*, $J = 8.6$, 2.3, 2 H). ^{13}C-NMR: 19.61; 32.86; 38.27; 118.79; 126.31; 127.97; 129.14; 132.08; 135.95; 175.45. HR-ESI-MS: 385.1385 ($[M+Na]^+$, $C_{19}H_{18}N_6NaO_2^+$; calc. 385.1389). Anal. calc. for $C_{19}H_{18}N_6O_2$ (362.39): C 62.97, H 5.01, N 23.19; found: C 62.83, H 5.04, N 22.96.

3-Benzyl-3,4-dihydro-1,2,3-benzotriazine (**4a**). Yellow solid. M.p. 80 – 82° (hexane/CH_2Cl_2). IR (KBr): 1425, 1098. ^{1}H-NMR: 4.22 (*s*, 2 H); 4.86 (*s*, 2 H); 6.82 (*d*, $J = 7.4$, 1 H); 7.23 (*td*, $J = 7.4$, 1.1, 2 H); 7.30 – 7.39 (*m*, 5 H); 7.46 (*dd*, $J = 8.0$, 1.1, 1 H). ^{13}C-NMR: 42.91; 60.41; 117.61; 125.35; 125.44; 128.12; 128.46; 128.78; 128.83; 129.50; 134.97; 126.91. HR-EI-MS: 223.1106 (M^+, $C_{14}H_{13}N_3^+$; calc. 223.1109). Anal. calc. for $C_{14}H_{13}N_3$ (223.27): C 75.31, H 5.87, N 18.82; found: C 75.02, H 5.84, N 18.67.

3-Benzyl-3,4-dihydro-4-methyl-1,2,3-benzotriazine (**4b**). *Representative Procedure.* Compound **1b** (0.48 g, 2.1 mmol) in THF (12 ml) at – 78° was treated with BuLi (1.6M in hexane; 2.1 mmol) as described for the preparation of **2a**. After BnBr (0.36 g, 2.1 mmol) was added, the temp. was gradually warmed to r.t. and stirring was continued overnight at the same temp. The resulting mixture was worked up as described for the preparation of **2a** and the crude product was purified by CC (SiO_2)

to afford **4b** (0.22 g, 44%). Yellow oil. R_f (AcOEt/hexane 1:4) 0.38. IR (neat): 1446, 1102. ^{1}H-NMR: 1.28 (*d*, $J = 6.3$, 3 H); 4.45 (*q*, $J = 6.3$, 1 H); 4.80 (*d*, $J = 14.9$, 1 H); 5.23 (*d*, $J = 14.9$, 1 H); 6.83 (*d*, $J = 7.4$, 1 H); 7.25 (*t*, $J = 7.4$, 1 H); 7.31 – 7.38 (*m*, 6 H); 7.48 (*d*, $J = 8.0$, 1 H). ^{13}C-NMR: 20.13; 48.16; 57.30; 122.77; 124.83; 128.02; 128.08; 128.51; 128.79; 128.81; 129.52; 135.83; 136.78. HR-ESI-MS: 238.1340 ($[M+H]^+$, $C_{15}H_{16}N_3^+$; calc. 238.1344). Anal. calc. for $C_{15}H_{15}N_3$ (237.30): C 75.92, H 6.37, N 17.71; found: C 76.00, H 6.41, N 17.51.

3-Benzyl-3,4-dihydro-4-phenyl-1,2,3-benzotriazine (**4c**). Yellow oil. R_f (AcOEt/hexane 1:5) 0.37. IR (neat): 1444, 1101. ^{1}H-NMR: 4.32 (*d*, $J = 14.9$, 1 H); 5.21 (*d*, $J = 14.9$, 1 H); 5.36 (*s*, 1 H); 6.67 (*d*, $J = 7.4$, 1 H); 7.14 (*td*, $J = 7.4$, 1.1, 1 H); 7.19 (*dd*, $J = 8.0$, 1.7, 2 H); 7.28 – 7.38 (*m*, 9 H); 7.53 (*dd*, $J = 8.0$, 1.1, 1 H). ^{13}C-NMR: 56.66; 57.46; 120.81; 125.55; 126.55; 127.55; 128.08; 128.49; 128.55; 128.75; 128.78; 129.03; 129.63; 135.15; 135.41; 141.52. HR-MS (DART): 300.1491 ($[M+H]^+$, $C_{20}H_{18}N_3^+$; calc. 300.1500). Anal. calc. for $C_{20}H_{17}N_3$ (299.37): C 80.24, H 5.72, N 14.04; found: C 80.00. H 5.73, N 13.86.

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