# 5-Substituted 2-alkyl- and 2-arylsulfonyliminohexahydro-1,3,5-triazines

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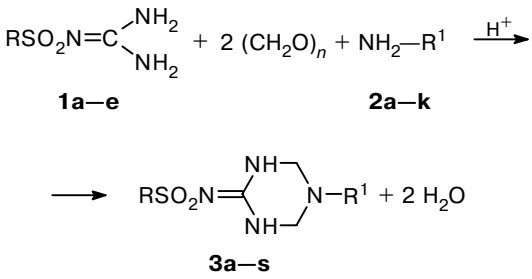
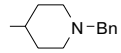
A new procedure was developed for the preparation of previously unknown 5-substituted 2-alkyl- and 2-arylsulfonyliminohexahydro-1,3,5-triazines by cyclocondensation of sulfoguanidines with formaldehyde and primary alkyl(aryl)amines.

**Key words:** 2-alkylsulfonyliminohexahydro-1,3,5-triazines, 2-arylsulfonyliminohexahydro-1,3,5-triazines, sulfoguanidines, amines, formaldehyde, cyclization, condensation.

In the last decade, a great variety of substituted 2-nitroiminohexahydro-1,3,5-triazines exhibiting high activities as insecticides and pesticides have been synthesized.[1] These compounds were prepared by the reactions of nitroguanidines with formaldehyde and primary amines. Taking into account that the $NO_2$ and $RSO_2$ groups exhibit similar electronic effects, one would expect that the application of an analogous scheme will afford the previously unknown 2-sulfonyliminohexahydro-1,3,5-triazines, which are promising reagents in the practical aspect, the more so as the sulfamide group is involved as a structural fragment in many compounds possessing useful biological activities.




| 1 | R | 2 | $R^1$ | 2 | $R^1$ |
|---|---|---|---|---|---|
| **a** | *p*-Tol | **a** | Me | **g** |  |
| **b** | 4-Me-3-$NO_2C_6H_3$ | **b** | All | | |
| **c** | 4-$AcNHC_6H_4$ | **c** | *cyclo*-$C_6H_{11}$ | **h** |  |
| **d** | 4-$NO_2C_6H_4$ | **d** | $CH_2CH_2OH$ | **i** | 4-$ClC_6H_4$ |
| **e** | Bu | **e** | $CH_2COONa$ | **j** | 4-$NO_2C_6H_4$ |
| | | **f** | Bn | **k** | 3-$NO_2C_6H_4$ |

In this connection, we found that the reactions of alkyl(aryl)sulfoguanidines (**1**) with formaldehyde (as paraformaldehyde) and primary amines (**2**) as mixtures of dry starting compounds (procedure *A*) or their solutions (suspensions) in MeCN (procedure *B*), which were performed generally in the presence of acid catalysts (TsOH or $ZnCl_2$) at 80—100 °C, gave rise to the desired 2-alkyl(aryl)sulfonyliminohexahydro-1,3,5-triazines (**3**). The yields of compounds **3** (13—72% with respect to the product recrystallized) depend substantially on both the type of the amine used and the type of sulfoguanidine.

The data on compounds **3a**—**s** are given in Table 1.

Amines characterized by rather high basicities, such as $R^2R^3CHNH_2$ ($R^2$ = H or Alk and $R^3$ = H, Alk, $CH_2OH$, $COO^-$, Ar, or Het), undergo cyclization most readily. In this case, cyclization proceeds more rapidly and affords products in higher yields (50—70%). Both TsOH and $ZnCl_2$ can be used as the catalyst. Generally, a catalyst is not needed in cyclization of aliphatic amines. On the contrary, cyclization with aromatic amines proceeds under more drastic conditions and requires strong acid (TsOH) as the catalyst.

The basicity of the N atoms in sulfoguanidine has analogous effects on the rate of cyclization and on the yields of **3**. Butylsulfoguanidine (**1e**) exhibits the highest reactivity. In the series of arylsulfoguanidines (**1a**—**d**), the reactivity decreases when electron-withdrawing substituents, such as AcNH or $NO_2$, are introduced into the core of the molecule, in particular, at the *para* position with respect to the $SO_2$ group.

If both arylsulfoguanidine and arylamine contain electron-withdrawing substituents, cyclization is most complicated. These reactions afford compounds **3** in low yields (10—30%) in spite of a twofold amount of TsOH used. The higher yields (30—40%) were achieved by performing the reactions in boiling anhydrous MeCN followed by azeotropic distillation of the mixture. The best results can be obtained by introducing an electron-withdrawing substituent into the aromatic core of compounds **3** as exemplified by the reaction of hexahydrotriazine **3i**.

The reactions of poorly reactive sulfoguanidines with aromatic amines gave rise to triarylhexahydro-1,3,5-triazines **4** along with compounds **3** and unconsumed **1**. The structures of compounds **4** were confirmed by $^1H$ NMR spectroscopy. In the presence of $ZnCl_2$ as the

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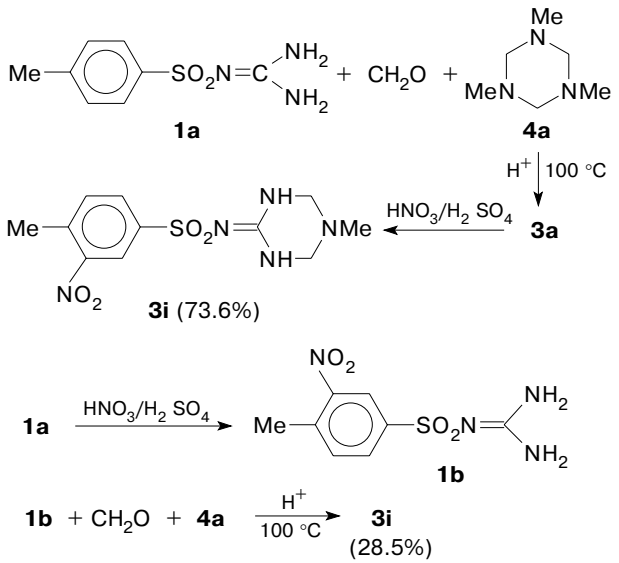
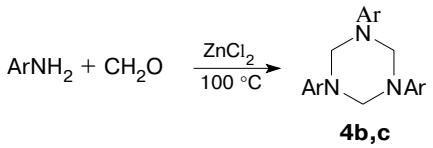


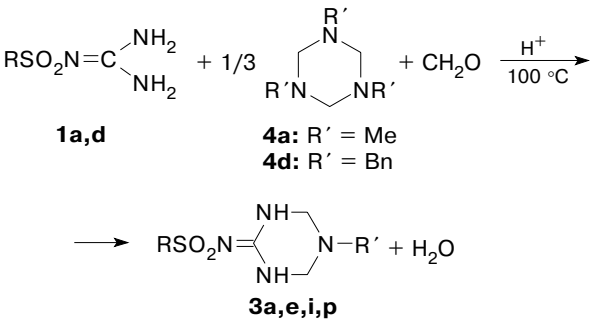
catalyst, the reactions took almost exclusively the latter path.



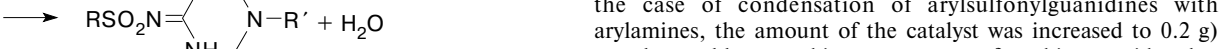
Ar = 4-$ClC_6H_4$ (**b**), 4-$NO_2C_6H_4$ (**c**)

The rapid disappearance of amines from the reaction mixture at the initial stage of cyclization accompanied by the simultaneous formation of **4b,c** suggests that the reactions with sulfoguanidines involve compounds **4b,c**, which are products of condensation of amines with formaldehyde.

Using the synthesis of compound **3e** as an example, it was demonstrated that cyclization of sulfoguanidines with **4b,c** (procedure *C*) afforded products in somewhat higher yields compared to those obtained according to the conventional scheme (59.1 and 54.7%, respectively). In addition, this reaction is a convenient synthetic procedure, which allows one to do away with gaseous and low-boiling amines as the starting reagents.



It should be noted that it is necessary to add one mole of $CH_2O$ to maintain the stoichiometric reagent ratio; otherwise the reaction mixture would contain a large amount of $R'NH_2$ resulting in a decrease in the yield of compounds **3** upon crystallization



The synthesized hexahydrotriazines **3** are high-melting crystalline compounds. Their melting is accompanied by decomposition. The structures of these compounds were confirmed by $^1H$ NMR spectroscopy.

Therefore, condensation of sulfoguanidines with primary alkyl(aryl)amines is a convenient procedure for the synthesis of the previously unknown 5-substituted 2-alkyl(aryl)sulfonyliminohexahydro-1,3,5-triazines.

## Experimental

The $^1H$ NMR spectra were recorded on Bruker WM-250 (250 MHz) and Bruker AM-300 (300 MHz) instruments. The $^1H$ NMR chemical shifts are given relative to the signal of the solvent (DMSO-$d_6$, 2.50 ppm). The melting points were determined on a Boetius stage. The course of the reactions and the purities of the products were monitored by TLC on Silufol UV-250 plates (a 1 : 2 : 7 MeOH—$C_6H_6$—$Et_2O$ system as the eluent).

Amines **2c,h,g,i** were purchased from Lancaster. The remaining amines and zinc chloride are commercial reagents (high purity or analytical grade) produced in Russia. Sulfoguanidines **1a,c,d** were synthesized according to known procedures.[2,3] 1,3,5-Trimethyl- (**4a**) and 1,3,5-tribenzylhexahydro-1,3,5-triazines (**4d**) were prepared according to procedures reported previously.[4,5]

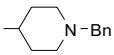
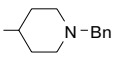
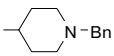
The characteristics of the resulting compounds are identical with those published in the literature. All reagents and solvents were used without additional purification or dryness, unless otherwise indicated.

**2-(4-Methyl-3-nitrophenylsulfonyl)guanidine (1b).** Compound **1a** (0.5 g, 2.35 mmol) was added portionwise to a mixture of concentrated $H_2SO_4$ (2.5 mL) and $HNO_3$ (*d* 1.47; 5 mL) cooled in an ice bath. The reaction mixture was stirred at 5 °C for 1 h and then poured onto crushed ice (20 g). The precipitate that formed was filtered off, washed several times with ice water, and dried in air. After crystallization of the residue (0.54 g), compound **1b** was obtained in a yield of 0.44 g (72.6%), m.p. 228—230 °C (96% EtOH). Found (%): C, 37.42; H, 3.88; S, 12.35. $C_8H_{10}N_4O_4S_1$. Calculated: C, 37.21; H, 3.90; S, 12.42. $^1H$ NMR, δ: 2.57 (s, 3 H, Me); 6.78 (br.s, 4 H, $NH_2$); 7.66 (d, 1 H, Ar, $J$ = 8.0 Hz); 7.96 (d, 1 H, Ar, $J$ = 8.0 Hz); 8.27 (s, 1 H, Ar). Compound **1b** was prepared analogously to **1a** [1] in 37.1% yield.

**2-Butylsulfonylguanidine (1e)** was prepared according to a procedure reported previously[2] analogously to compound **1a** in 70.3% yield, m.p. 163—165 °C (EtOH) (*cf.* lit. data:[6] 158—159 °C). $^1H$ NMR, δ: 0.87 (t, 3 H, Me, $J$ = 7.3 Hz); 1.28—1.45 and 1.53—1.68 (both m, 2 H each, $CH_2$); 2.83 (t, 2 H, $CH_2SO_2$, $J$ = 7.9 Hz); 6.57 (br.s, 4 H, $NH_2$).

**Preparation of 5-substituted 2-alkyl(aryl)sulfonyliminohexahydro-1,3,5-triazines (3).** ***Procedure A.*** A mixture of alkyl(aryl)sulfonylguanidine **1a—e** (10 mmol), $(CH_2O)_n$ (24 mmol), amine **2b—k** (10 mmol), and $TsOH \cdot H_2O$ (0.1 g; in the case of condensation of arylsulfonylguanidines with arylamines, the amount of the catalyst was increased to 0.2 g) was thoroughly ground in a mortar, transferred into a wide tube, which was placed into a boiling bath, and heated for 1—4 h until an aqueous condensate ceased to form at the tube edges (TLC control was additionally performed). The sintered mixture was triturated with $Et_2O$ (10—20 mL), transferred to a porous filter, and washed successively with $Et_2O$ (10 mL) and $Me_2CO$

**Table 1.** Procedures for the preparation of compounds **3a—s** and their characteristics

| Compound | R | $R^1$ | Procedure for the preparation | Yield* (%) | M.p./°C (solvent) | Found / Calculated (%) C | H | Cl | N | S | Molecular formula |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **3a** | *p*-Tol | Me | *C* | 74.5 | 203—205 | 49.31 | 5.94 | | 21.06 | 11.74 | $C_{11}H_{16}N_4O_2S$ |
| | | | | 58.7 | (50% EtOH) | 49.24 | 6.01 | | 20.88 | 11.95 | |
| **3b** | *p*-Tol | All | *A* | 91.2 | 178—180 | 53.21 | 6.08 | | 18.80 | 10.71 | $C_{13}H_{18}N_4O_2S$ |
| | | | | 72.1 | (50% EtOH) | 53.04 | 6.16 | | 19.03 | 10.89 | |
| **3c** | *p*-Tol | $CH_2CH_2OH$ | *A* | 58.7 | 169—171 | 48.23 | 6.18 | | 18.63 | 10.65 | $C_{12}H_{18}N_4O_3S$ |
| | | | | 40.1 | (96% EtOH) | 48.31 | 6.08 | | 18.78 | 10.75 | |
| **3d** | *p*-Tol | $CH_2COONa$ | *A* | 95.8 | 209—212 | 42.95 | 4.55 | | 16.63 | 9.71 | $C_{12}H_{15}N_4NaO_4S$ |
| | | | | 65.9 | (50% EtOH) | 43.11 | 4.52 | | 16.76 | 9.59 | |
| **3e** | *p*-Tol | Bn | *A* | 64.5 | 200—202 | 59.35 | 6.10 | | 16.22 | 9.28 | $C_{17}H_{20}N_4O_2S$ |
| | | | | 54.7 | | 59.28 | 5.85 | | 16.27 | 9.31 | |
| | | | *C* | 69.8 | (50% EtOH) | | | | | | |
| | | | | 59.1 | | | | | | | |
| **3f** | *p*-Tol |  | *A* | 88.9 | 203—205 | 61.66 | 6.60 | | 16.48 | 7.43 | $C_{22}H_{29}N_5O_2S$ |
| | | | | 57.5 | (96% EtOH) | 61.80 | 6.84 | | 16.38 | 7.50 | |
| **3g** | *p*-Tol | 4-$ClC_6H_4$ | *A* | 44.0 | 273—275 | 52.79 | 4.89 | 9.74 | 15.54 | 8.81 | $C_{16}H_{17}Cl_1N_4O_2S$ |
| | | | | 24.2 | | 52.67 | 4.70 | 9.72 | 15.36 | 8.79 | |
| | | | *B* | 60.3 | (DMSO) | | | | | | |
| | | | | 40.2 | | | | | | | |
| **3h** | *p*-Tol | 3-$NO_2C_6H_4$ | *A* | 79.8 | 264—266 | 50.99 | 4.55 | | 18.70 | 8.44 | $C_{16}H_{17}N_5O_4S$ |
| | | | | 43.7 | | 51.19 | 4.56 | | 18.66 | 8.54 | |
| | | | *B* | 82.9 | (DMSO) | | | | | | |
| | | | | 50.0 | | | | | | | |
| **3i** | 4-Me-3-$NO_2C_6H_3$ | Me | *C* | 39.2 | 211—213 | 42.16 | 5.05 | | 22.50 | 10.22 | $C_{11}H_{15}N_5O_4S$ |
| | | | | 21.6 | (50% EtOH) | 42.17 | 4.83 | | 22.35 | 10.23 | |
| **3j** | 4-Me-3-$NO_2C_6H_3$ | 4-$ClC_6H_4$ | *A* | 42.7 | 245—247 | 46.79 | 4.03 | 8.74 | 17.15 | 7.91 | $C_{16}H_{16}Cl_1N_5O_4S$ |
| | | | | 28.5 | (DMSO) | 46.89 | 3.94 | 8.65 | 17.09 | 7.82 | |
| **3k** | 4-$AcNHC_6H_4$ | All | *A* | 81.5 | 200—202 | 49.89 | 5.66 | | 20.98 | 9.32 | $C_{14}H_{19}N_5O_2S$ |
| | | | | 65.2 | (96% EtOH) | 49.84 | 5.68 | | 20.76 | 9.50 | |
| **3l** | 4-$AcNHC_6H_4$ | *cyclo*-$C_6H_{11}$ | *A* | 84.0 | 225—227 | 53.85 | 6.64 | | 18.14 | 8.36 | $C_{17}H_{25}N_5O_3S$ |
| | | | | 61.6 | (50% EtOH) | 53.81 | 6.64 | | 18.46 | 8.45 | |
| **3m** | 4-$AcNHC_6H_4$ |  | *A* | 93.5 | 201—203 | 58.79 | 6.39 | | 17.74 | 6.93 | $C_{23}H_{30}N_6O_3S_1$ |
| | | | | 56.1 | (96% EtOH) | 58.70 | 6.43 | | 17.86 | 6.81 | |
| **3n** | 4-$AcNHC_6H_4$ | 4-$ClC_6H_4$ | *A* | 39.2 | 278—280 | 50.08 | 4.67 | 8.62 | 17.43 | 7.79 | $C_{17}H_{18}Cl_1N_5O_3S_1$ |
| | | | | 20.6 | | 50.06 | 4.45 | 8.69 | 17.17 | 7.86 | |
| | | | *B* | 45.1 | (DMSO) | | | | | | |
| | | | | 29.6 | | | | | | | |
| **3o** | 4-$AcNHC_6H_4$ | 4-$NO_2C_6H_4$ | *A* | 38.2 | 285—287 | 48.91 | 4.39 | | 20.01 | 7.66 | $C_{17}H_{18}N_6O_5S_1$ |
| | | | | 20.0 | | 48.80 | 4.34 | | 20.08 | 7.66 | |
| | | | *B* | 79.3 | (DMSO) | | | | | | |
| | | | | 47.8 | | | | | | | |
| **3p** | 4-$NO_2C_6H_4$ | Me | *C* | 33.4 | 191—193 | 40.12 | 4.48 | | 23.61 | 10.63 | $C_{10}H_{13}N_5O_4S_1$ |
| | | | | 13.4 | (50% EtOH) | 40.13 | 4.38 | | 23.40 | 10.71 | |
| **3q** | Bu |  | *A* | 61.0 | 198—200 | 47.99 | 6.66 | | 18.37 | 10.71 | $C_{12}H_{20}N_4O_3S_1$ |
| | | | | 31.1 | (50% EtOH) | 47.98 | 6.71 | | 18.65 | 10.67 | |
| **3r** | Bu |  | *A* | 86.1 | 219—221 | 58.19 | 7.98 | | 17.83 | 8.20 | $C_{19}H_{31}N_5O_2S_1$ |
| | | | | 51.8 | (96% EtOH) | 57.99 | 7.94 | | 17.80 | 8.15 | |
| **3s** | Bu | 4-$ClC_6H_4$ | *A* | 65.0 | 238—240 | 47.23 | 5.88 | 10.38 | 16.71 | 9.39 | $C_{13}H_{19}ClN_4O_2$ |
| | | | | 51.1 | (96% EtOH) | 47.20 | 5.79 | 10.72 | 16.94 | 9.69 | |

* The ratio between the raw product and the product obtained after recrystallization.

(2—3 times, 20 mL). The raw product was dried in air and recrystallized from the corresponding solvent (see Table 1) to obtain compounds **3b—h**; **j—o**, and **p—s**.

***Procedure B.*** A mixture of arylsulfonylguanidine **1a,c** (10 mmol), $(CH_2O)_n$ (24 mmol), arylamine **2i—k** (10 mmol), and $TsOH \cdot H_2O$ (0.2 g) in anhydrous MeCN (100 mL; prepared by distillation over $P_2O_5$) was refluxed for 1—2 h. Then the solvent was slowly distilled off under atmospheric pressure to ~1/3 of the initial volume. The resulting suspension was cooled to ~20 °C. The precipitate was filtered off, washed with

MeCN, and dried in air. Compounds **3g,h,n,o** were obtained after crystallization from the corresponding solvent (see Table 1).

***Procedure C.*** A mixture or arylsulfonylguanidine **1a,b,d** (10 mmol), $(CH_2O)_n$ (12 mmol), and $TsOH \cdot H_2O$ (0.1 g) or $ZnCl_2$ (0.1 g) was thoroughly ground in a mortar and transferred into a wide tube. Then a solution of trihexahydro-1,3,5-triazine (**4a,b**) (3.3 mmol) in $Et_2O$ (1—2 mL) was added to the reaction mixture. After removal of $Et_2O$ on a warm water bath, the tube was transferred into a boiling water bath. Subsequent operations were carried out as described in procedure *A*.

Compounds **3a,e,i,p** were obtained.

The physicochemical and spectral characteristics of the corresponding hexahydrotriazines **3** prepared according to different procedures are identical.

**5-Methyl-2-*p*-tosyliminohexahydro-1,3,5-triazine (3a).** $^1$H NMR, δ: 2.28 (s, 3 H, MeN); 2.34 (s, 3 H, MeAr); 4.03 (s, 4 H, $NCH_2N$); 7.28 and 7.67 (both d, 2 H each, Ar, $J$ = 8.0 Hz); 7.55 (br.s, 2 H, NH).

**5-Allyl-2-*p*-tosyliminohexahydro-1,3,5-triazine (3b).** $^1$H NMR, δ: 2.34 (s, 3 H, Me); 3.03 (d, 2 H, $CH_2$—CH=$CH_2$, $J$ = 4.8 Hz); 4.08 (s, 4 H, $NCH_2N$); 5.00—5.18 (m, 2 H, CH=$CH_2$); 5.65—5.88 (m, 1 H, CH); 7.28 and 7.69 (both d, 2 H each, Ar, $J$ = 8.1 Hz); 7.57 (br.s, 2 H, NH).

**5-(2-Hydroxyethyl)-2-*p*-tosyliminohexahydro-1,3,5-triazine (3c).** $^1$H NMR, δ: 2.34 (s, 3 H, Me); 2.53 (t, 2 H, N$CH_2CH_2$, $J$ = 4.7 Hz); 3.48 (br.t, 2 H, $CH_2CH_2O$, $J$ = 4.7 Hz); 4.12 (s, 4 H, $NCH_2N$); 4.55 (br.s, 1 H, OH); 7.28 and 7.67 (both d, 2 H each, Ar, $J$ = 8.0 Hz); 7.58 (br.s, 2 H, NH).

**Sodium (2-*p*-tosyliminohexahydro-1,3,5-triazin-5-yl)acetate (3d).** $^1$H NMR, δ: 2.34 (s, 3 H, Me); 3.00 (s, 2 H, $CH_2CO$); 4.07 (s, 4 H, $NCH_2N$); 7.28 and 7.67 (both d, 2 H each, Ar, $J$ = 8.0 Hz); 7.75 (br.s, 2 H, NH).

**5-Benzyl-2-*p*-tosyliminohexahydro-1,3,5-triazine (3e).** $^1$H NMR, δ: 2.36 (s, 3 H, Me); 3.56 (s, 2 H, $CH_2$Ph); 4.08 (s, 4 H, $NCH_2N$), 7.34—7.48 (m, 5 H, Ph); 7.28 and 7.71 (both d, 2 H each, $C_6H_4$Me, $J$ = 8.2 Hz); 7.63 (br.s, 2 H, NH).

**5-[1-Benzylpiperidin-1-yl]-2-*p*-tosyliminohexahydro-1,3,5-triazine (3f).** $^1$H NMR, δ: 1.20—1.42, 1.59—1.84, and 2.15—2.30 (all m, 7 H, 3 $CH_2$, CH of piperidine); 2.37 (s, 3 H, Me); 2.67—2.81 (m, 2 H, $CH_2$ of piperidine); 3.39 (s, 2 H, $CH_2$Ph); 4.18 (s, 4 H, $NCH_2N$); 7.21 and 7.65 (both d, 2 H each, $C_6H_4$Me, $J$ = 8.1 Hz); 7.22—7.32 (m, 5 H, Ph); 7.58 (br.s, 2 H, NH).

**5-(4-Chlorophenyl)-2-*p*-tosyliminohexahydro-1,3,5-triazine (3g).** $^1$H NMR, δ: 2.36 (s, 3 H, Me); 4.72 (s, 4 H, $CH_2N$); 7.07 and 7.25 (both d, 2 H each, $C_6H_4Cl$, $J$ = 8.9 Hz); 7.20 and 7.55 (both d, 2 H each, $C_6H_4$Me, $J$ = 8.1 Hz); 7.86 (br.s, 2 H, NH).

**5-(3-Nitrophenyl)-2-*p*-tosyliminohexahydro-1,3,5-triazine (3h).** $^1$H NMR, δ: 2.30 (s, 3 H, Me); 4.87 (s, 4 H, $NCH_2N$); 7.12 (d, 2 H, $C_6H_4$Me, $J$ = 8.1 Hz); 7.47—7.61 and 7.74—7.91 (both m, 6 H, H arom.); 7.96 (br.s, 2 H, NH).

**5-Methyl-2-(4-methyl-3-nitrophenylsulfonyl)iminohexahydro-1,3,5-triazine (3i).** $^1$H NMR, δ: 2.29 (s, 3 H, MeN); 2.57 (s, 3 H, Me); 4.05 (s, 4 H, $NCH_2N$); 7.65 (d, 1 H, Ar, $J$ = 8.3 Hz); 7.69 (br.s, 2 H, NH); 7.98 (d, 1 H, Ar, $J$ = 8.3 Hz); 8.30 (s, 1 H, Ar).

**5-(4-Chlorophenyl)-2-(4-methyl-3-nitrophenylsulfonyl)iminohexahydro-1,3,5-triazine (3j).** $^1$H NMR, δ: 2.58 (s, 3 H, Me); 4.75 (s, 4 H, $NCH_2N$); 7.01 and 7.19 (both d, 2 H each, $C_6H_4Cl$, $J$ = 8.5 Hz); 7.54 (d, 1 H, $C_6H_3$Me, $J$ = 8.3 Hz); 7.84 (d, 1 H, $C_6H_3$Me, $J$ = 8.3 Hz); 7.97 (s, 2 H, NH); 8.24 (s, 1 H, $C_6H_3$Me).

**2-(4-Acetamidophenylsulfonyl)-5-allyliminohexahydro-1,3,5-triazine (3k).** $^1$H NMR, δ: 2.07 (s, 3 H, Me); 3.03 (d, 2 H, $CH_2$CH=$CH_2$, $J$ = 4.8 Hz); 4.09 (s, 4 H, $NCH_2N$); 5.02—5.20 (m, 2 H, CH=$CH_2$); 5.65—5.88 (m, 1 H, CH=$CH_2$); 7.57 (br.s, 2 H, NH of the ring); 7.69 (s, 4 H, Ar); 10.21 (s, 1 H, CONH).

**2-(4-Acetamidophenylsulfonyl)imino-5-cyclohexylhexahydro-1,3,5-triazine (3l).** $^1$H NMR, δ: 0.87—1.17 and 1.41—1.81 (both m, 10 H, $CH_2$ of cyclohexane); 2.07 (s, 3 H, Me); 2.15—2.27 (m, 1 H, CH of cyclohexane); 4.19 (s, 4 H, $NCH_2N$); 7.51 (br.s, 2 H, NH of the ring); 7.69 (s, 4 H, Ar); 10.20 (s, 1 H, CONH).

**2-(4-Acetamidophenylsulfonyl)imino-5-(1-benzylpiperidin-4-yl)hexahydro-1,3,5-triazine (3m).** $^1$H NMR, δ: 1.19—1.40 and 1.58—1.85 (both m, 6 H, $CH_2$ of piperidine); 2.07 (s, 3 H, Me); 2.10—2.30 (m, 1 H, CH of piperidine); 2.64—2.84 (m, 2 H, $CH_2$ of piperidine); 3.38 (s, 2 H, $CH_2$Ph); 4.18 (s, 4 H, $NCH_2N$); 7.15—7.35 (m, 5 H, Ph); 7.50 (br.s, 2 H, NH of the ring); 7.65 (s, 4 H, $C_6H_4SO_2$); 10.10 (s, 1 H, CONH).

**2-(4-Acetamidophenylsulfonyl)imino-5-(4-chlorophenyl)hexahydro-1,3,5-triazine (3n).** $^1$H NMR, δ: 2.09 (s, 3 H, Me); 4.71 (s, 4 H, $NCH_2N$); 7.03 and 7.22 (both d, 2 H each, $C_6H_4Cl$, $J$ = 8.7 Hz); 7.63 (s, 4 H, $C_6H_4SO_2$); 7.80 (br.s, 2 H, NH of the ring); 10.18 (s, 1 H, CONH).

**2-(4-Acetamidophenylsulfonyl)imino-5-(4-nitrophenyl)hexahydro-1,3,5-triazine (3o).** $^1$H NMR, δ: 2.08 (s, 3 H, Me); 4.89 (s, 4 H, $NCH_2N$); 7.20 and 8.08 (both d, 2 H each, $C_6H_4NO_2$, $J$ = 9.1 Hz); 7.59 (s, 4 H, $C_6H_4SO_2$); 7.89 (br.s, 2 H, NH of the ring); 10.03 (s, 1 H, CONH).

**5-Methyl-2-(4-nitorphenylsulfonyl)iminohexahydro-1,3,5-triazine (3p).** $^1$H NMR, δ: 2.38 (s, 3 H, Me); 4.05 (s, 4 H, $NCH_2N$); 7.75 (br.s, 2 H, NH); 8.05 and 8.35 (both d, 2 H each, Ar, $J$ = 8.8 Hz).

**2-Butylsulfonylimino-5-[(2-furyl)methyl]hexahydro-1,3,5-triazine (3q).** $^1$H NMR, δ: 0.88 (t, 3 H, Me; $J$ = 7.0 Hz); 1.30—1.73 (m, 4 H, $CH_2$ of the chain); 2.85 (t, 2 H, $CH_2$ of the chain, $J$ = 7.7 Hz); 3.77 (s, 2 H, $CH_2$Het); 4.13 (s, 4 H, $NCH_2N$); 6.34 (d, 1 H, Het, $J$ = 8.6 Hz); 6.40—6.46 (m, 1 H, Het); 7.49 (br.s, 2 H, NH); 7.61 (s, 1 H, Het).

**5-(1-Benzylpiperidin-4-yl)-2-butylsulfonyliminohexahydro-1,3,5-triazine (3r).** $^1$H NMR, δ: 0.92 (t, 3 H, Me, $J$ = 7.2 Hz); 1.30—2.06 (m, 10 H, 2 $CH_2$ of the chain, 3 $CH_2$ of piperidine); 2.55—2.92 (m, 5 H, $CH_2$ of the chain, $CH_2$, CH of piperidine); 3.43 (s, 2 H, $CH_2$Ph); 4.23 (s, 4 H, $NCH_2N$); 7.15—7.35 (m, 5 H, Ph); 7.42 (br.s, 2 H, NH).

**2-Butylsulfonylimino-5-(4-chlorophenyl)hexahydro-1,3,5-triazine (3s).** $^1$H NMR, δ: 0.8 (t, 3 H, Me, $J$ = 7.0 Hz); 1.14—1.60 (m, 4 H, $CH_2$ of the chain); 2.75 (t, 2 H, $CH_2$ of the chain, $J$ = 7.6 Hz); 4.77 (s, 4 H, $NCH_2N$); 7.18 and 7.35 (both d, 2 H each, Ar, $J$ = 8.5 Hz); 7.65 (br.s, 2 H, NH).

**Nitration of compound 3a.** Compound **3a** (0.54 g, 2 mmol) was added portionwise to a mixture of concentrated $H_2SO_4$ (2.5 mL) and $HNO_3$ (d 1.47; 5 mL) cooled in an ice bath. The reaction mixture was stirred at 5 °C for 1 h and then poured onto crushed ice (20 g). The precipitate that formed was filtered off, washed several times with ice water, and dried in air. After crystallization from 50% EtOH, compound **3i** was obtained in a yield of 0.46 g (73.6%), m.p. 211—213 °C.

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