Deoxygenative vs. Vicarious Nucleophilic Substitution of Hydrogen in Reactions of 1,2,4-Triazine 4-Oxides with Æ-Halocarbanions

Dmitry N. Kozhevnikov,*[a] Vladimir L. Rusinov,[a] Oleg N. Chupakhin,[a] Mieczyslaw Makosza,[b] Andrzej Rykowski,[c] and Ewa Wolinska[c]

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The 3,6-diaryl-1,2,4-triazine 4-oxides **1a–e** undergo a nucleophilic substitution of hydrogen with the α-halomethyl aryl sulfones **2, 3** and **7** by two alternative pathways: vicarious nucleophilic substitution (VNS) and/or an intramolecular deoxygenative process. The former pathway is found to dominate in the reaction of **1** with bromomethyl tolyl sulfone (**7**) yielding the 5-tosylmethyl-1,2,4-triazine 4-oxides **6**, while the reaction with the chloromethyl aryl sulfones **2** and **3** leads to the 5-arylsulfonylchloromethyl-1,2,4-triazines **4** and **5**, respectively, as the products of deoxygenative substitution. The reaction of 6-phenyl-1,2,4-triazine 4-oxide (**1f**) with the chloromethyl aryl sulfones **2** and **3** proceeds differently. At low temperature (–75 C) the products of the VNS reaction at position 5 (**6f** and **12f**) are formed. At room temperature the 7-chloro-1-hydroxy-3-phenyl-7-(arylsulfonyl)-1,4,5-triazahepta-1,3,6-trienes **10f** and **11f** are obtained by addition of the carbanions **2** and **3** in the 3-position, followed by the ring opening of the resulting σ adduct.

Introduction

Nucleophilic substitution of hydrogen (S_N^H) is a versatile tool for the introduction of a variety of substituents into electrophilic carbo- and heterocyclic arenes.[1] This process proceeds as a two step reaction: addition of nucleophilic agents to electrophilic rings in positions occupied by hydrogen to produce σ^H adducts and further conversion of these σ^H adducts into the products of S_N^H.[2,3] Amongst many variants of the nucleophilic substitution of hydrogen, one of the most general appears to be vicarious nucleophilic substitution (VNS), which proceeds when the reacting nucleophiles contain leaving groups X at the nucleophilic center. The σ^H adducts formed by such nucleophiles undergo a base-induced β-elimination of HX giving anions of the final products.[4] Another important variant of the S_N^H process is conversion of the σ^H adducts into products by oxidative processes which can proceed upon action of an external oxidant.[5] Both of these reactions proceed readily with 1,2,4-triazines. Thus, the treatment of substituted triazines with α-halocarbanions results in VNS at the 5-position. When this position is occupied the substitution takes place at the 3-position.[6] Oxidative nucleophilic substitution of hydrogen proceeds readily in 1,2,4-triazines; for example, amination with a solution of $KMnO_4$ in liquid ammonia.[7] It is well-known that introduction of the *N*-oxide group to aza heterocycles not only increases the electrophilicity of the hetarene, but provides the possibility of aromatization of the σ^H adducts by elimination of the hydrogen together with the oxygen of the *N*-oxide group as a molecule of water, alcohol or carboxylic acid (deoxygenative S_N^H).[8] Despite the difference in the mechanism this variant of aromatization can be considered as an oxidation due to the change of oxidation levels from the reagents to the products. In this case the *N*-oxide group plays the role of a formal internal oxidant. This intramolecular oxidative pathway of aromatization of the σ^H adducts is particularly efficient in the reaction of nucleophiles with 1,2,4-triazine *N*-oxides.[9] One could therefore expect that reactions of α-halocarbanions with 1,2,4-triazine 4-oxides can proceed along two competing pathways: VNS and deoxygenative S_N^H, both of these processes being different transformations of the common intermediate σ^H adduct. In the present paper studies of the competition between these reactions as a function of reactants and conditions are reported.

[a] Urals State Technical University, Department of Organic Chemistry,
620002, Ekaterinburg, Russia
Fax: (internat.) + 7-3432/740-458
E-mail: rusinov@htf.ustu.ru
[b] Institute of Organic Chemistry Polish Academy of Sciences,
POB 58, 01-224 Warsaw 42, Poland
Fax: (internat.) + 48-22/632-6681
E-mail: icho-s@icho.edu.pl
[c] Institute of Chemistry, University of Podlasie,
08-110, Siedlce, Poland
E-mail: rykowski@ap.siedlce.pl

Results and Discussion

When 1,2,4-triazine 4-oxides (**1a–e**), in which the 3- and 6-positions are occupied with aryl substituents, were treated

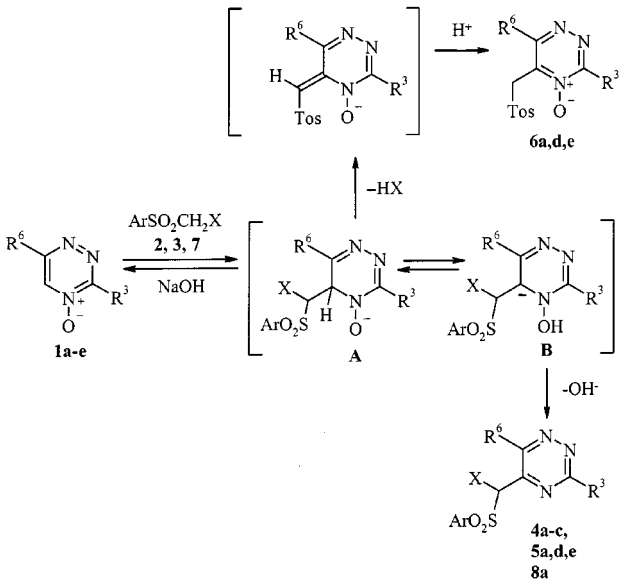
with carbanions of chloromethyl phenyl and *p*-tolyl sulfones **2** and **3**, generated in situ in the presence of an excess of finely powdered NaOH in DMF at room temperature (conditions A, Table 1), the major process was deoxygenative replacement of the hydrogen in the 5-position. The products, the 5-(α-chloro-α-arylsulfonylmethyl)-1,2,4-triazines **4a−c, 5a,d,e** were isolated in 64−89% yields. The expected competing VNS reaction giving 5-arylsulfonylmethyl-1,2,4-triazine 4-oxides was a minor process, and the products of VNS (**6a,d**) could be isolated in low yields in a few cases (Table 1). Both of these reactions proceed via a common intermediate σ^H adduct of the carbanions **2** and **3** at C-5 of the triazine ring. Further conversion of this σ^H adduct by base-induced β-elimination of HCl results in VNS, whereas an intramolecular redox process, apparently via protonation of the *N*-oxide oxygen and dehydration, gives the products of deoxygenative substitution **4a−c** (see Scheme 1).

Table 1. The reaction conditions and yields of **4**, **6−12**

Triazine 4-oxide	Sulfone	X	Ar	Conditions[a]	Products of S_N^H (Yield)[b] Deoxygenative	VNS
1a	**2**	Cl	Ph	A	**4a** (78%)	
1a	**3**	Cl	Tol	A	**5a** (72%)	**6a** (4%)
				D	**5a** (70%)	**6a** (6%)
				E	**5a** (65%)	**6a** (traces)
				F	**5a** (50%)	
1a	**7**	Br	Tol	A	**8a** (7%)	**6a** (61%)
1a	**7**	Br	Tol	A	**8a** (4%)	**6a** (67%)
1a	**7**	Br	Tol	B	**8a** (74%)	
1b	**2**	Cl	Ph	A	**4b** (89%)	
1c	**2**	Cl	Ph	A	**4c** (85%)	
1d	**3**	Cl	Tol	A	**5d** (64%)	**6d** (5%)
1d	**7**	Br	Tol	A		**6d** (68%)
1e	**3**	Cl	Tol	A	**5e** (67%)	
1e	**7**	Br	Tol	A		**6e** (42%)
1f	**2**	Cl	Ph	C		**12f** (49%)
1f	**3**	Cl	Tol	C		**6f** (28%)

[a] A: NaOH, DMF, room temp.; B: i) *t*BuOK, THF/DMF, −75 °C, ii) HOAc, −75 °C, iii) Ac_2O; C: *t*BuOK, THF, −75 °C; D: *t*BuOK (excess), DMF, room temp.; E: *t*BuOK (excess), DMF, −40 °C; F: *t*BuOK (equiv.), DMF, room temp. [b] Isolated yield.

Formation of the VNS products, although in small amounts, indicates that there are no large differences between the rates of these competing reactions. Nevertheless, changes in the reaction conditions (type, amount and concentration of base, solvents and temperature) have no visible effect on this competition. Thus the use of an excess of *t*BuOK in DMF at room temperature (conditions D, Table 1) or at −40 °C (conditions E, Table 1) in the reaction of **1a** with chloromethyltolylsulfone (**3**) leads to the same products **5a** (main product) and **6a** (minor product). When the starting materials **1a** and **3** in DMF are treated with an equimolar amount of *t*BuOK at room temperature (conditions F, Table 1), only the substituted 1,2,4-triazine **5a** is obtained, and in lower yield (50%). Although according to the stoichiometry in the reaction **1a** + **3** → **5a** base is not



$R^3 = R^6 = C_6H_5$ (a); R^3 = 4-ClC_6H_4, $R^6 = C_6H_5$ (b); R^3 = 2,4-$Cl_2C_6H_4$, $R^6 = C_6H_5$ (c); R^3 = 4-$NO_2C_6H_4$, $R^6 = C_6H_5$ (d); $R^3 = C_6H_5$, R^6 = 4-$CH_3C_6H_4$ (e); Ar = Ph, X = Cl (**2**, **4**); Ar = Tol, X = Cl (**3**, **5**, **6**); Ar = *p*-Tol, X = Br (**7**, **6**, **8**)

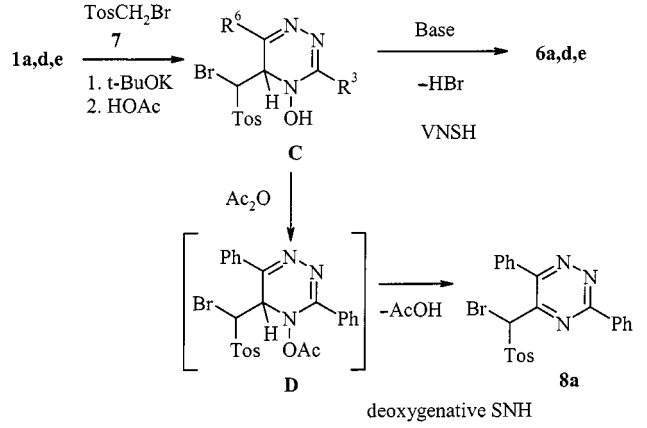
Scheme 1

consumed, the product **5a**, being a strong CH acid, is deprotonated upon formation and therefore more than one equivalent of base should be used. Indeed, in the presence of catalytic amounts (0.1 equiv.) of *t*BuOK in DMF most of the starting 1,2,4-triazine 4-oxide **1a** was reisolated from the reaction mixture. The same result (no reaction) was observed using NEt_3 as a base.

We expected that the reaction of the carbanion of bromomethyl tolyl sulfone (**7**) with the 1,2,4-triazine 4-oxides could proceed via the VNS pathway because β-elimination of HBr from the σ^H adduct should proceed much faster than HCl from the analogous σ^H adducts of **2** or **3**. Indeed, the reaction of **1a,d,e** with **7** carried out in the presence of NaOH in DMF (conditions A, Table 1) gave mainly the 5-tosylmethyl-1,2,4-triazines 4-oxides **6a,d,e** as products of the VNS reaction. The product, 5-(α-bromo-α-tosylmethyl)-1,2,4-triazine (**8a**), of the deoxygenative transformation of the σ^H adduct was obtained as a minor component (7%) only in the reaction of **1a** with **7**. Thus the outcome of the reaction of carbanions of halomethyl aryl sulfones with substituted 1,2,4-triazines 4-oxides is governed by the type of halogen: chloromethyl sulfones react along the deoxygenative pathway whereas bromomethyl sulfone undergoes a VNS. The selection of the reaction course depends on the relative rates of β-elimination of hydrogen halides from the σ^H adducts and dehydration (see Scheme 1).

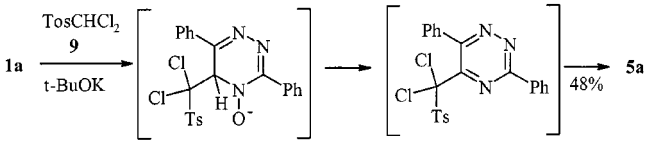
It is, however, possible to perform the deoxygenative replacement of hydrogen in 1,2,4-triazine 4-oxides with the carbanion of bromomethyl sulfone by an intramolecular process. Addition of the carbanion generated from **7** and *t*BuOK to **1a** at −75°C followed by quenching at this temperature with acetic acid (conditions B, Table 1) gave the σ^H adduct as a crystalline product that is insufficiently stable to

be identified by spectroscopic methods. Treatment of this adduct with *t*BuOK gave the VNS product **6a** by elimination of HBr. However, when this adduct was treated with acetic anhydride, the product of a deoxygenative transformation − 5-(α-bromo-α-tosylmethyl)-3,6-diphenyl-1,2,4-triazine (**8a**) − was obtained (see Scheme 2). Similar deoxygenative transformations of σ^H adducts to 1,2,4-triazine 4-oxides upon treatment with benzoyl chloride have been reported previously.[10]



Scheme 2

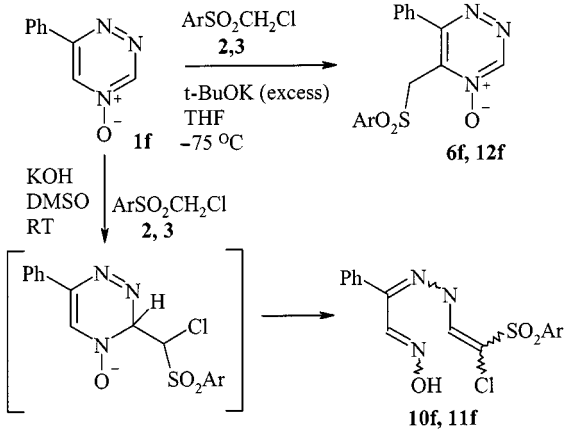
The transformation by β-elimination of HX should proceed faster for the σ^H adducts of carbanions containing two halogens due to statistical effects. However, reaction of the carbanion generated from dichloromethyl phenyl sulfone (**9**) with **1a** (conditions A, Table 1) gave 2,6-diphenyl-5-(chlorophenylsulfonylmethyl)-1,2,4-triazine (**5a**) (see Scheme 3). The reaction apparently proceeded by deoxygenative conversion of the σ^H adduct, giving the dichloromethylsulfone, which was then dehalogenated under the reaction conditions. Such halophilic-type reactions are common for polyhalo compounds, particularly polyhalosulfones.[11,12] An alternative method of transformation of the σ^H adduct, namely base-induced β-elimination of HCl followed by deoxygenation of the VNS product, is much less feasible (see Scheme 3).



Scheme 3

Interestingly, the reaction of carbanions of chloromethyl aryl sulfones with 6-aryl-1,2,4-triazine 4-oxides that have both the 3- and 5-positions available for nucleophilic addition proceeds differently. Treatment of 6-phenyl-1,2,4-triazine 4-oxide (**1f**) with **2** or **3** in DMSO in the presence of an excess of KOH at room temperature (conditions G, see Exp. Sect.) resulted in formation of the open chain products **10f** and **11f**. Formation of these products can be rationalized by addition of the carbanion at the 3-position of the heterocycle followed by ring opening of the intermediate σ^H adduct C. Such ring opening transformations of anionic σ^H adducts of nucleophiles at the 3-position of 1,2,4-triazine 4-oxides are often observed.[10]

When **1f** and **2** were reacted in the presence of *t*BuOK in THF at −75 °C (condition C, Table 1) the product of the VNS reaction at the 5-position i.e. 6-phenyl-5-(phenylsulfonylmethyl)-1,2,4-triazine 4-oxide (**12f**) was formed in moderate yield. In a similar manner the reaction of **1f** with **3** gave the VNS product 6-phenyl-5-[(*p*-tolylsulfonyl)methyl]-1,2,4-triazine 4-oxide (**6f**) (see Scheme 4).



Ar = Ph (**10f, 12f**); Ar = *p*-Tol (**6f, 11f**)

Scheme 4

The absence of an aryl substituent R^3 at the 3-position of 1,2,4-triazine 4-oxides makes nucleophilic attack at this position possible and opens up another pathway for the reaction, namely heterocyclic ring opening in the intermediate σ^H adduct.

The change of reaction pathway between the ring opening proceeding via the σ^H adduct at C-3 at room temperature and deoxygenative substitution of hydrogen via the σ^H adduct at C-5 at −75°C can be rationalized in terms of kinetic and thermodynamic reaction control. It has already been shown[13] that nucleophilic addition at C-5 of 1,2,4-triazine 4-oxide proceeds faster than at C-3; at higher temperature the system equilibrates rapidly to produce σ^H adducts at C-3, which, once formed, can be converted into stable open-chain products by the ring opening process.

Conclusions

Carbanions of halomethyl aryl sulfones can react with substituted 1,2,4-triazine-4-oxides along at last three pathways. Addition at C-5 produces σ^H adducts, which are converted into final products according to intramolecular redox stoichiometry so deoxygenative substitution takes

place, or by base-induced β-elimination of HX giving products of vicarious nucleophilic substitution VNS. On the other hand, σ^H adducts produced by addition at C-3 undergo a ring opening to give acylic hydrazine derivatives. The reaction course can be controlled by changing the type of halogen in the sulfones, the substituents of the 1,2,4-triazines and the reaction conditions.

Experimental Section

General Remarks: ^{1}H NMR spectra were measured on Bruker WM-250 (250.1 MHz) or on a Varian Gemini (200 MHz) spectrometer, in [D_6]DMSO (if not specially marked). Mass-spectra were measured on a Varian MAT-311 or an AMD 604 spectrometer (electron impact 70 eV).

The starting 1,2,4-triazine 4-oxides were synthesized according to a procedure published earlier.[14] The sulfones were either commercially available (**2**, **3**) or prepared by known methods: bromomethyl tolylsulfone (**7**),[15] dichloromethyl tolylsulfone (**9**).[16]

Reaction of 1,2,4-Triazine 4-oxides (1a−e) with Carbanions. Method A: A solution of the corresponding 1,2,4-triazine 4-oxide (1 mmol) and the carbanion precursor (1.1 mmol) in DMF (2−3 mL) was added dropwise to a vigorously stirred suspension of finely powdered NaOH (1.0 g) in DMF (3 mL) at 0 °C. The reaction mixture was stirred at room temperature for 1−3 h, then poured into dilute hydrochloric acid and extracted with CH_2Cl_2. The organic layer was separated, dried with $MgSO_4$ and the solvents evaporated. The residue was purified by column chromatography (silica gel, CH_2Cl_2) and recrystallised from ethanol or acetic acid.

Method B: A solution of the corresponding 1,2,4-triazine 4-oxide (1 mmol) and the carbanion precursor (1.1 mmol) in THF (2−3 mL) was added dropwise to a vigorously stirred solution of freshly sublimed *t*BuOK (560 mg, 5 mmol) in THF/DMF (3 mL) at −75 °C. The reaction mixture was stirred at this temperature for 30 min, then quenched with 0.5 mL of acetic acid and poured into water. The crystals were filtered, washed with acetone and dried. The σ-adducts obtained by this manner were dissolved in DMF (3 mL) containing 0.5 mL of acetic anhydride. The mixture was refluxed for 15 min and the solvents were then removed in vacuo. The residue was recrystallised from acetic acid.

Method C: A solution of 6-phenyl-1,2,4-triazine 4-oxide (173 mg, 1 mmol) and the carbanion precursor **2** or **3** (2 mmol) in THF (8 mL) was added drop wise at −75 °C to a solution of *t*BuOK (700 mg, 6 mmol) in THF (8 mL). The mixture was stirred at −75 °C for 2.5 h and then quenched with solid ammonium chloride at 0 °C. The solvent was removed in vacuo. The products **6f** and **12f** were isolated by column chromatography (silica gel, chloroform) and recrystallised from ethanol.

Method D: A solution of the 1,2,4-triazine 4-oxide **1a** (250 mg, 1 mmol) and the sulfone **3** (225 mg, 1.1 mmol) in DMF (2 mL) was added dropwise to a vigorously stirred solution of *t*BuOK (560 mg, 5 mmol) in DMF (3 mL) at 0 °C. The reaction mixture was stirred at room temperature for 1 h, then poured into dilute hydrochloric acid and worked up as above.

Method E: See method D; temperature: −40 °C for 3 h.

Method F: A solution of the 1,2,4-triazine 4-oxide **1a** (250 mg, 1 mmol) and the sulfone **3** (225 mg, 1.1 mmol) in DMF (2 mL) was added dropwise to a vigorously stirred solution of *t*BuOK (115 mg, 1 mmol) in DMF (2 mL) at 0 °C. The reaction mixture was stirred at room temperature for 2 h, then poured into dilute hydrochloric acid and worked up as above.

5-[Chloro(phenylsulfonyl)methyl]-3,6-diphenyl-1,2,4-triazine (4a): M.p. 136−138 °C, ^{1}H NMR: δ = 6.26 (s, 1 H), 7.5−7.7 (m, 8 H), 7.7−7.9 (m, 5 H), 8.2 (m, 2 H). MS: *m*/*z* (%) = 423 (1) and 421 (3) [M^+]. $C_{22}H_{16}ClN_3O_2S$ (421.9): calcd. C 62.63, H 3.82, N 9.96; found C 62.80, H 3.96, N 10.11.

3-(4-Chlorophenyl)-5-[chloro(phenylsulfonyl)methyl]-6-phenyl-1,2,4-triazine (4b): M.p. 172−174 °C, ^{1}H NMR: δ = 6.28 (s, 1 H), 7.5−7.9 (m, 12 H), 8.2 (m, 2 H). MS: *m*/*z* (%) = 457 (1) and 455 (3) [M^+]. $C_{22}H_{15}Cl_2N_3O_2S$ (456.3): calcd. C 57.90, H 3.31, N 9.21; found C 57.98, H 3.22, N 9.45.

3-[2,4-Di(chloro)phenyl]-5-[chloro(phenylsulfonyl)methyl]-6-phenyl-1,2,4-triazine (4c): M.p. 138−140 °C, ^{1}H NMR: δ = 6.33 (s, 1 H, CH), 7.5−7.9 (m, 13 H). $C_{22}H_{14}Cl_3N_3O_2S$ (490.8): calcd. C 53.84, H 2.88, N 8.56; found C 54.01, H 2.80, N 8.70.

5-[Chloro(*p*-tolylsulfonyl)methyl]-3,6-diphenyl-1,2,4-triazine (5a): Yield: 72%; m.p. 170−171 °C. ^{1}H NMR: δ = 2.41 (s, 3 H, CH_3), 6.47 (s, 1 H, CH), 7.38 (m, 2 H), 7.50−7.80 (m, 10 H), 8.15 (m, 2 H). $C_{23}H_{18}ClN_3O_2S$ (435.9): calcd. C 63.37, H 4.16, Cl 8.13, N 9.64, S 7.36; found C 63.38, H 3.95, Cl 8.11, N 9.70, S 7.49.

5-[Chloro(*p*-tolylsulfonyl)methyl]-3-(4-nitrophenyl)-6-phenyl-1,2,4-triazine (5d): M.p. 195−196 °C. ^{1}H NMR: δ = 2.41 (s, 3 H, CH_3), 6.56 (s, 1 H, CH), 7.35 (m, 2 H), 7.55 (m, 2 H), 7.62−7.81 (m, 5 H), 8.38 (m, 2 H), 8.45 (m, 2 H). $C_{23}H_{17}ClN_4O_4S$ (480.9): calcd. C 57.44, H 3.56, Cl 7.37, N 11.65, S 6.66; found C 57.49, H 3.40, Cl 7.39, N 11.54, S 6.64.

5-[Chloro(*p*-tolylsulfonyl)methyl]-6-(*p*-tolyl)-3-phenyl-1,2,4-triazine (5e): M.p. 168−169 °C. ^{1}H NMR: δ = 2.42 (s, 3 H, CH_3), 2.46 (s, 3 H, CH_3), 6.46 (s, 1 H, CH), 7.30−7.70 (m, 11 H), 8.13 (m, 2 H). $C_{24}H_{20}ClN_3O_2S$ (450.0): calcd. C 64.06, H 4.48, N 9.34, S 7.13; found C 64.21, H 4.60, N 9.58, S 7.26.

3,6-Diphenyl-5-[(*p*-tolylsulfonyl)methyl]-1,2,4-triazine 4-oxide (6a): M.p. 179−180 °C. ^{1}H NMR: δ = 2.39 (s, 3 H, CH_3), 5.04 (s, 2 H, CH_2), 7.34 (m, 2 H), 7.50−7.70 (m, 10 H), 8.03 (m, 2 H). $C_{23}H_{19}N_3O_3S$ (417.5): calcd. C 66.17, H 4.59, N 10.06, S 7.68; found C 65.98, H 4.75, N 9.78, S 7.63.

3-(4-Nitrophenyl)-6-phenyl-5-[(*p*-tolylsulfonyl)methyl]-1,2,4-triazine 4-Oxide (6d): M.p. > 280 °C. ^{1}H NMR: δ = 2.39 (s, 3 H, CH_3), 5.07 (s, 2 H, CH_2), 7.30−7.36 (m, 2 H), 7.50−7.70 (m, 7 H), 8.25−8.45 (m, 4 H). $C_{23}H_{18}N_4O_5S$ (462.5): calcd. C 59.73, H 3.92, N 12.11; found C 59.60, H 3.81, N 11.95.

3-Phenyl-6-(*p*-tolyl)-5-[(*p*-tolylsulfonyl)methyl]-1,2,4-triazine 4-Oxide (6e): M.p. 188−189 °C. ^{1}H NMR: δ = 2.39 (s, 3 H, CH_3), 2.42 (s, 3 H, CH_3), 5.05 (s, 2 H, CH_2), 7.30−7.38 (m, 4 H), 7.50−7.70 (m, 7 H), 8.02 (m, 2 H). $C_{24}H_{21}N_3O_3S$ (431.5): calcd. C 66.80, H 4.91, N 9.74, S 7.43; found C 66.67, H 4.74, N 9.77, S 7.33.

6-Phenyl-5-[(*p*-tolylsulfonyl)methyl]-1,2,4-triazine 4-Oxide (6f): M.p. 151−152 °C. ^{1}H NMR ($CDCl_3$): 2.47 (s, 3 H, CH_3), 4.87 (s, 2 H, CH_2), 7.30−7.37 (m, 2 H), 7.50−7.80 (m, 7 H), 9.27(s,1 H). HR LSIMS (NBA): *m*/*z* = 342.09147 (calcd. 342.09124 for $C_{17}H_{16}N_3O_3S$). $C_{17}H_{15}N_3O_3S$ (341.4): calcd. C 59.82, H 4.39, N 12.31; found C 59.71, H 4.34, N 12.30.

5-[Bromo(*p*-tolylsulfonyl)methyl]-3,6-diphenyl-1,2,4-triazine (8a): M.p. 169−170 °C. ^{1}H NMR: δ = 2.43 (s, 3 H, CH_3), 6.33 (s, 1 H,

CH), 7.38 (m, 2 H), 7.50−7.70 (m, 10 H), 8.23 (m, 2 H). $C_{23}H_{18}BrN_3O_2S$ (480.4): calcd. C 57.51, H 3.78, Br 16.63, N 8.75, S 6.68; found C 57.48, H 3.63, Br 16.50, N 8.85, S 6.68.

6-Phenyl-5-(phenylsulfonylmethyl)-1,2,4-triazine 4-Oxide (12f): M.p. 155−156 °C. ^{1}H NMR ($CDCl_3$): δ = 4.88 (s, 2 H, CH_2), 7.50−7.75 (m, 8 H), 7.87−7.94 (m, 2 H), 9.27 (s, 1 H). HR LSIMS (NBA): *m/z* = 328.07656 (calcd. 328.07559 for $C_{16}H_{14}N_3O_3S$). $C_{16}H_{13}N_3O_3S·H_2O$ (345.4): C 55.65, H 4.34, N 12.17; found C 55.63, H 3.97, N 12.04.

Synthesis of the Open-Chain Adducts (10f, 11f). Method G: A solution of 6-phenyl-1,2,4-triazine 4-oxide (173 mg, 1 mmol) and the carbanion precursor **2** or **3** (1.1 mmol) in DMSO (8 mL) was added dropwise to a vigorously stirred suspension of finely powdered KOH (1.4 g) in DMSO (8 mL) at room temperature. The reaction mixture was stirred at this temperature for 1.5 h, then poured into ice/water and neutralized with acetic acid. The precipitated solid was filtered, washed with water and purified by column chromatography (silica gel, chloroform).

7-Chloro-1-hydroxy-3-phenyl-7-(phenylsulfonyl)-1,4,5-triazahepta-1,3,6-triene (10f): Yield 10%, m.p. 172−174 °C. ^{1}H NMR: δ = 7.4−7.7 (m, 8 H), 7.9−8.0 (m, 2 H), 8.31 (d, *J* = 10.3 Hz, 1 H), 8.32 (s, 1 H), 12.00 (d, *J* = 10.3 Hz, 1 H). HRMS EI (70 eV): *m/z* = 363.0443 (calcd. 363.0444 for $C_{16}H_{14}{}^{35}ClN_3O_3S$). $C_{16}H_{14}ClN_3O_3S$ (363.8): calcd. C 52.89, H 3.85, N 11.57; found C 52.79, H 3.86, N 11.05.

7-Chloro-1-hydroxy-3-phenyl-7-(*p*-tolylsulfonyl)-1,4,5-triazahepta-1,3,6-triene (11f): Yield 24%, m.p. 184−186 °C. ^{1}H NMR: δ = 2.43 (s, 3 H, CH_3), 7.25−7.7.48 (m, 8 H), 7.9−8.0 (m, 2 H), 8.08 (br. s, 1 H, OH), 8.31 (d, *J* = 10.3 Hz, 1 H), 8.32 (s, 1 H), 12.00 (d, *J* = 10.3 Hz, 1 H, NH). HRMS EI (70 eV): *m/z* = 377.0607 (calcd. 377.0601 for $C_{17}H_{16}{}^{35}ClN_3O_3S$). $C_{17}H_{16}ClN_3O_3S$ (377.8): calcd. C 54.11, H 4.24, N 11.14; found C 53.89, H 4.21, N 10.90.

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