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Novel Applications of N-Sulfonyl-alkylamines in [2+4] Cycloadditions

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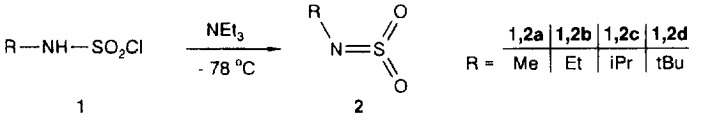
Dedicated to Professor Hans Suschitzky on the occasion of his 80th birthday

Abstract: N-Sulfonylamine **2c** was generated from the corresponding sulfamoyl chloride **1c** at - 78 °C by triethylamine-induced dehydrohalogenation or from the novel precursor **5** with a phthalimidyl leaving group at room temperature. Trapping of **2c** from either source with 3-trimethylsiloxy-1,3-butadiene (**3**) gave the expected [2+4] cycloadduct **4**. However, the reaction of N-sulfonyl-alkylamines **2** with 2-aza-1,3-dienes **7** depended on the size of the alkyl group in **2** and on the reaction conditions. Thus, use of the heterocumulenes **2a,b** (alkyl residue = Me, Et) at - 78 °C gave rise to the cycloadducts **8a,b** regioselectively. In contrast, the reaction of **7** with **2c,d** carrying a bulky isopropyl or tert.-butyl group provided the bissulfamoylated 2-aza-1,3-dienes **10a-c**. On the other hand, starting from precursor **5** at room temperature also **2c** reacted with the dienes **7** to form the ring-closure products **8c,d**.

N-Sulfonylamines are highly electrophilic heterocumulenes.[1] But the free compounds, especially the N-alkyl derivatives, can not be isolated nor are they stable enough for handling at ambient temperature in solution. So far, the most elegant and convenient method for the *in situ*-generation of N-sulfonyl-alkylamines **2** is the dehydrohalogenation of the corresponding sulfamoyl chlorides **1** using triethylamine at - 78 °C.[1-3]

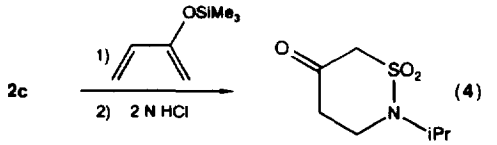


1 2

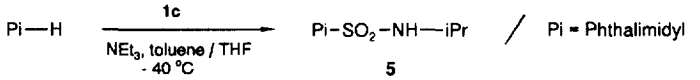
	1,2a	1,2b	1,2c	1,2d
R =	Me	Et	iPr	tBu

Probably due to their comparatively low reactivity under these conditions, only one report[4] of a successful application of **2** as dienophile in a formal [2+4] cycloaddition with the strongly nucleophilic dienes 2,4-bis-(trimethylsiloxy)-1,3-pentadiene and 1-methoxy-3-trimethylsiloxy-1,3-butadiene yielding 1,1-dioxo-2*H*-1,2-thiazine-5-ones has been published.

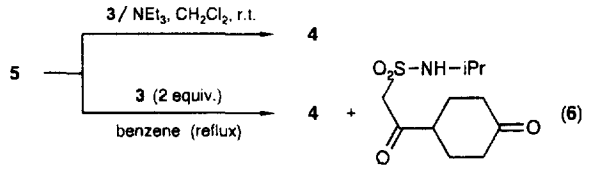
We have observed that similar reaction conditions also allow a formal Diels Alder reaction between N-sulfonyl-isopropylamine (**2c**), from **1c**, and the moderately activated diene **3** to give the perhydro-1,1-dioxo-1,2-thiazine-5-one **4** in dichloromethane between -78 °C and room temperature.



An efficient method for the *in situ*-generation of very reactive synthetic intermediates, such as thioaldehydes[5], thionitrosoarenes[6], or α-oxothiones[7], is based on the fragmentation of appropriate phthalimidyl derivatives. We therefore turned our attention to N-alkylsulfamoyl phthalimides, which should undergo fragmentation to give phthalimide and N-sulfonylamines **2** at elevated temperatures or by the action of base at room temperature. In fact, the heterocumulene precursor **5** was accessible by treatment of a 1:1 mixture of phthalimide and triethylamine with **1c**. However, even if an excess of **1c** was employed, we obtained **5** along with unreacted phthalimide (0.28 - 0.1 equiv.). As the latter should be generated together with **2c** during the subsequent manipulations, we used these mixtures without further purification.

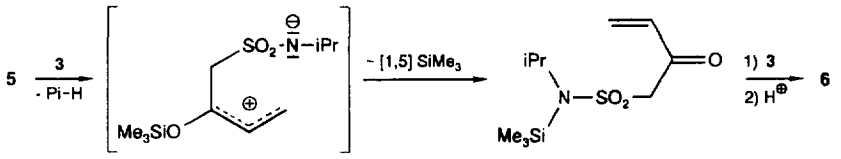


In fact, **2c** could be trapped as cycloadduct **4** from the triethylamine-induced generation of **5** employing an equimolar amount of diene **3**. On the other hand, if the precursor **5** was heated in benzene in the presence of two equivalents of **3**, but in the absence of a base, this provided the cyclohexanone **6** (21 %) together with detectable amounts of **4**.



A plausible mechanism for the formation of **6** involves thiophilic attack of diene **3** via the activated C(1) atom on the *in situ*-generated intermediate **2c**, subsequent [1,5] migration of the trimethylsilyl group from O to N, followed by regiospecific [2+4] cycloaddition, and finally desilylation (Scheme 1).

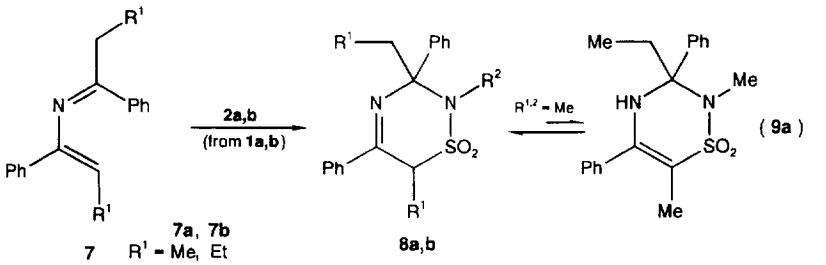
Scheme 1. Probable Pathway to **6**

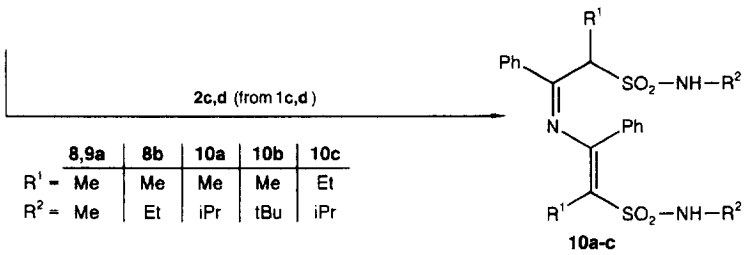


Finally, we explored the suitability of 2-aza-1,3-dienes **7** to intercept N-sulfonyl-alkylamines giving [2+4] cycloadducts. It is well established[8-10] that dienes of type **7**, which have been found to be poorly activated 4π compounds, are useful reagents for trapping electrophilic heterocumulenes, such as isocyanates or isothiocyanates, to give six-membered heterocycles. In the reaction with N-sulfonyl-alkylamines **2**, we have found that the course of the transformation is strongly influenced by steric effects and the reaction conditions. Thus, when **2a,b** as generated by dehydrohalogenation of **1a,b** at -78 °C, were treated with **7** this resulted in

the expected mixtures of diastereomers **8a,b** along with the corresponding NH-tautomer **9a** (Table 1).Thus, the sp^2-nitrogen in **7** sufficiently activates the diene and also controls the regioselectivity of product formation. The formation of diastereomers may indicate a stepwise cycloaddition, but the configurational integrity of precursor **7** canot be taken for granted.

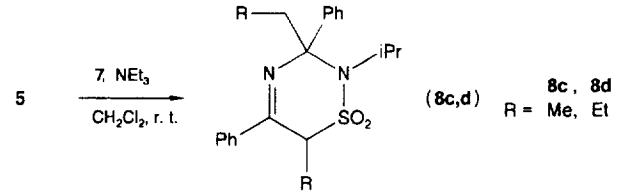
In contrast, heterocumulenes **2c,d** carrying bulky alkyl groups reacted with **7** to yield exclusively the yellow bissulfamoylated 2-aza-1,3-dienes **10**, in spite of using equimolar amounts of starting materials. Cycloadducts or monoacylated products could not be isolated. Addition of catalytic amounts of the Lewis acid boron trifluoride diethyl etherate did not influence the reaction course, except for increased yields of **10** (Table 1).





	8,9a	8b	10a	10b	10c
R^1 =	Me	Me	Me	Me	Et
R^2 =	Me	Et	iPr	tBu	iPr

However, treatment of **2c**, as generated by triethylamine-mediated fragmentation of **5**, with **7** provided modest amounts of the [2+4] cycloadducts **8c,d** at room temperature.



In conclusion, it is possible to intercept N-sulfonyl-alkylamines with 1,3-dienes, even with moderately or poorly activated derivatives to form [2+4] cycloadducts, but one must take into consideration the possibility to form acyclic products with sulfamoyl moieties, such as **6** or **10**. Thus, multistage mechanisms via dipolar intermediates are apparently favored over concerted hetero Diels-Alder reactions (cf. also ref.[4]).

Support of this work by BASF AG and by Fonds der Chemischen Industrie, Frankfurt, is gratefully acknowledged.

EXPERIMENTAL

General. Melting points are uncorrected and were taken on a Büchi melting point apparatus. Elemental analyses were carried out by Institut für Pharmazeutische Chemie, Technische Universität Braunschweig. NMR spectra (^{1}H NMR: 400 MHz, ^{13}C NMR: 100 MHz) were measured on a Bruker ARX-400 spectrometer relative to internal TMS. IR spectra were recorded on a PYE UNICAM SP3-200 spectrometer. For column chromatography (CC) Merck silica gel 60 (70-230 mesh) was used. PE = petroleum ether, EA = ethyl acetate. The reported reactions were carried out under anhydrous nitrogen and using dried and distilled solvents.

Sulfamoyl chlorides **1a-d** were provided by BASF AG. 2-Aza-1,3-dienes **7a,b**[11] were obtained from the appropriate ketimine[12] precursors according to literature instructions.

Perhydro-2-isopropyl-1,1-dioxo-1,2-thiazine-5-one (**4**): To a stirred solution of **3** (0.569 g, 4 mmol) in dichloromethane (5 ml) triethylamine (0.67 ml, 4.8 mmol) and, subsequently, **1c** (630 mg, 4 mmol) were slowly added at - 78 °C. Then the mixture was allowed to warm to room temperature within approx. 6 h and stirred for additional 2 h. After shaking with 2 N HCl (10 ml) for 30 min dichloromethane (200 ml) was added and the phases were separated. The organic layer was washed twice with water (50 ml) and dried ($MgSO_4$). Finally, the solvent was evaporated and the crude oil was subjected to CC using PE/EA (1/1). Yield 0.105 g (14 %), m. p. 92 - 92.5 °C, colorless crystals. - IR (KBr): υ = 2950 cm^{-1}, 2895, 2860, 1747, 1317, 1230, 1170, 1123, 908. - ^{1}H NMR ($CDCl_3$): δ = 1.27 [d, J = 6.8 Hz, 6 H, $(CH_3)_2CH$], 2.63 (t, J = 6.2 Hz, 2 H, CH_2-C=O), 3.41 (t, J = 6.2 Hz, 2 H, CH_2-N), 3.94 (s, 2 H, CH_2-SO_2), 4.46 (sept, J = 6.8 Hz, 1 H, CH). - ^{13}C NMR ($CDCl_3$): δ = 21.03 (CH_3), 36.21 (CH_2-C=O), 41.00 (CH_2-N), 47.98 (CH), 65.55 (CH_2-SO_2), 195.55 (C=O). - $C_7H_{13}NO_3S$ (191.25): calcd. C 43.96, H 6.85, N 7.32, S 16.76, found C 44.04, H 6.80, N 7.15, S 16.73.

N-(Isopropylsulfamoyl)-phthalimide (**5**): A vigorously stirred suspension of powdered phthalimide (4.41 g, 30 mmol) in toluene (100 ml) was treated with triethylamine (4.17 ml, 30 mmol) and then cooled to - 40 °C. Subsequently, **1c** (4.73 g, 30 mmol) was added dropwise over 30 min at this temperature and after stirring for 1 h the mixture was slowly diluted with THF (50 ml) at - 40 to - 35 °C (internal temperature). After additional stirring for 2 h and slow (over approx. 4 h) warming to room temperature, the solvents were evaporated in vacuum. The crude product was dissolved in dichloromethane (300 ml), washed twice with ice water (20 ml) and dried ($MgSO_4$). Filtration, evaporation of dichloromethane and recrystallization (dichloromethane/PE) led to solid materials, viz. **5** along with phthalimide (0.28 - 0.1 equiv.) according to ^{1}H NMR measurements). E. g.: Yield 6.89 g (includes 0.1 equiv. phthalimide, yield of **5**: 82 %), m. p. 145.5 °C, colorless crystals. - IR (KBr): υ = 3295 cm^{-1}, 2960, 2915, 2855, 1785, 1733, 1373, 1263, 1190, 1164, 1142, 1039, 1017, 706. - ^{1}H NMR ($CDCl_3$): δ = 1.24 [d, J = 6.6 Hz, 6 H, $(CH_3)_2CH$], 3.77 (sept, J = 6.6 Hz, 1 H, CH), 5.49 (br. d, J = 6.6 Hz, 1 H, HN), 7.86, (dd, 2 H, aromatic H), 7.97 (dd, 2 H, aromatic H). - ^{13}C NMR ($CDCl_3$): δ = 23.01 (CH_3), 47.92 (CH), 124.60 (aromatic CH), 130.93 (aromatic C), 135.51 (aromatic CH), 164.12 (C=O). - $C_{11}H_{12}N_2O_4S$ (268.29), elemental analysis was carried out with a 3.5:1 mixture of **5**/phthalimide, as obtained in a typical experiment: calcd. according to this mixture C 51.42, H 4.36, N 10.32, S 10.33, found C 51.51, H 4.33, N 10.00, S 10.36.

Perhydro-2-isopropyl-1,1-dioxo-1,2-thiazine-5-one (**4**) *employing precursor* **5**: To a stirred mixture of **3** (0.427 g, 3 mmol) and partially dissolved **5** (0.805 g, 3 mmol) in dichloromethane (5 ml) triethylamine (0.42

ml, 3 mmol) was added within 30 min at room temperature. The progress of the reaction was indicated by complete dissolution of **5** and, after an induction period, by beginning precipitation of phthalimide. Stirring for 12 h completed the transformation. After diluting with dichloromethane (100 ml) the mixture was shaken with 2 N HCl (20 ml) for 30 min at room temperature and the phases were separated. The organic layer was washed twice with water (10 ml) and dried ($MgSO_4$). Then the solvent was distilled off and the crude product was subjected to CC using PE/EA (1/1) to give **4** [98 mg (17 %), for analytical and spectroscopic properties cf. above].

N-Isopropyl-2-oxo-2-(4-oxo-cyclohexyl)-ethanesulfonamide (**6**): A mixture of **5** (0.537 g, 2 mmol) and the diene **3** (0.569 g, 4 mmol) was refluxed in benzene (5 ml) for 20 h. Work-up was carried out as above in the corresponding base-induced reaction. CC using PE/EA (3/2) as eluent gave: 1st fraction (0.117 g), a mixture of several compounds, containing the heterocycle **4** as established by NMR spectroscopy (cf. above). 2nd fraction (**6**): Yield 0.11 g (21 %), m. p. 98 - 99 °C (EA/PE), colorless crystals. - IR (KBr): υ = 3195 cm^{-1}, 2950, 2920, 2895, 2865, 2840, 1710, 1700 (sh), 1328, 1165, 1134, 1021, 908. - ^1H NMR ([D6]DMSO): δ = 1.11 [d, J = 6.5 Hz, 6 H, $(CH_3)_2CH$], 1.68, 2.15 [2 m, 4 H, $CH(CH_2)_2$], 2.25, 2.40 [2 m, 4 H, $(CH_2)_2C{=}O$], 3.12 (tt, J = 10.6, 3.4 Hz, 1 H, C*H*-C=O), 3.49 [sept, J = 6.6 Hz, 1 H, $(CH_3)_2CH$], 4.41 (s, 2 H, CH_2-SO_2), 7.30 (d, J = 7.2 Hz, 1 H, *H*NCH). - ^{13}C NMR ([D6]DMSO): δ = 23.88 (CH_3), 27.24 (CH_2CH), 39.45 (CH_2-C=O), 45.56 (*C*H-CH_3), 47.65 (*C*H-C=O), 61.78 (CH_2-SO_2), 202.35 (exocycl. *C*=O), 209.77 (cycl. *C*=O). - $^1H,^1H$- and $^1H,^{13}C$-COSY measurements verify the assignment of specified peaks. - $C_{11}H_{19}NO_4S$ (261.34): calcd. C 50.56, H 7.33, N 5.36, S 12.27, found C 50.73, H 7.51, N 5.37, S 12.28.

***Trapping of N-Sulfonylamines* (2), *generated from Sulfamoyl chlorides* (1), *with 2-Aza-1,3-dienes* (7)** - *General procedure*: To a stirred solution of 7 in dichloromethane (3 ml/mmol 7) were added slowly and dropwise, sequentially, triethylamine (1.2 equiv.) and the sulfamoyl chloride **1** (1 equiv.), in the case of solid **1d** as concentrated solution in dichloromethane, at -78 °C. The mixture was stirred for 1 h and then brought to room temperature within approx. 6 h. After additional stirring for 2 h, dichloromethane (100 ml) was added. This solution was washed twice with water (10 ml), dried ($MgSO_4$) and concentrated for CC. For yields and significant analytical as well as spectroscopic data of the isolated products **8-10** see Table 1.

Mixture of *3-Ethyl-2,6-dimethyl-3,5-diphenyl-3,6-dihydro-2H-1,2,4-thiadiazine-1,1-dioxide* [**8a**, 2 diastereomers (labeled "x,y" below)] and *3-Ethyl-2,6-dimethyl-3,5-diphenyl-3,4-dihydro-2H-1,2,4-thiadiazine-1,1-dioxide* [**9a** (labeled "z" below)] in a 1:1:1 ratio as obtained from 5 mmol **1a** (0.65 g) and **7a** (1.25 g): CC using PE/EA (15/1), colorless crystals (EA/cyclohexane). - ^1H NMR ($CDCl_3$): δ = 0.65^z (t, J = 7.2 Hz, 3 H, CH_3CH_2), 0.99^x, 1.11^y (t, J = 7.2 Hz, 3 H, CH_3CH_2), 1.67^x, 1.70^y (d, J = 7.1 Hz, 3 H, CH_3CH), 1.90^z (s, 3 H, CH_3C-6), 2.24, 2.40, 2.66 (m, 2 H, $CH_3CH_2)^{x,y,z}$, 2.72, 2.76, 3.04 (s, 3 H, $CH_3N)^{x,y,z}$, 4.37^x, 4.44^y (q, J = 7.1 Hz, 1 H, CH_3CH), 4.48^z (br. s, 1 H, *H*N), 7.23-7.51, 7.84 (several m, 10 H, aromatic H)^{x,y,z}. Listed numbers of hydrogen atoms refer to respective isomer. ^{13}C NMR ($CDCl_3$): δ = 8.91, 9.17^{x,y}, 9.75^z (CH_3CH_2), 11.11^z, 16.16, 16.37^{x,y} (CH_3C-6), 27.14 $(CH_2)^z$, 27.61, 28.59 $(CH_3N)^{x,y}$, 33.28, 33.46 $(CH_2)^{x,y}$, 33.86 $(CH_3N)^z$, 52.77 (HC-6)^{x,y}, 79.60^z, 86.04, 87.09^{x,y} (quart. *C*-3), 126.02, 126.84, 126.86, 127.11, 127.45, 127.77, 127.91, 128.12, 128.26, 128.50, 128.59, 128.75, 128.80, 128.98, 129.89, 129.89, 131.03, 131.10 (aromatic *C*H)^{x,y,z}, 135.26, 136.36, 136.41, 138.32, 139.24, 139.42 (aromatic C)^{x,y,z}.

2,3-Diethyl-6-methyl-3,5-diphenyl-3,6-dihydro-2H-1,2,4-thiadiazine-1,1-dioxide [**8b**, 2 diastereomers, ratio 4.5:1], obtained from 5.6 mmol **1b** (0.804 g) and **7a** (1.4 g): CC using PE/EA (5/1), colorless crystals

Table 1. Trapping Products of N-Sulfonylamines (**2**) with 2-Aza-1,3-dienes (**7**)

	Fp [°C]	Yield [%]	^{13}C-δ ($CDCl_3$) [ppm]			IR (KBr): υ [cm^{-1}]		Analysis calcd. (found)			
			C=N	C=*C*-N	*C*=C-N			C	H	N	S
8a / **9a**[a]	132-138	28	157.79, 159.01	143.31	103.49	3305, 3030, 2955, 2905, 2850, 1650, 1612, 1317, 1300, 1145, 763, 701.	$C_{19}H_{22}N_2O_2S$ (342.46)	66.64 (66.40)	6.48 (6.47)	8.18 (8.13)	9.36 (10.08)
8b[b]	138-141	53	157.79[c]	-	-	3060, 3030, 2955, 2910, 2850, 1649, 1318, 1306, 1138, 1000, 768, 692.	$C_{20}H_{24}N_2O_2S$ (356.48)	67.39 (67.53)	6.79 (6.79)	7.86 (7.82)	8.99 (9.06)
8c	143-144	26	159.17	-	-	3030, 2950, 2905, 2840, 1640, 1303, 1157, 1135, 986, 753, 685.	$C_{21}H_{26}N_2O_2S$ (370.51)	68.08 (67.92)	7.07 (7.05)	7.56 (7.53)	8.65 (8.70)
8d	122-123	21	158.84	-	-	3045, 2955, 2920, 2860, 1642, 1300, 1288, 1157, 1128, 1010, 755, 683.	$C_{23}H_{30}N_2O_2S$ (398.56)	69.31 (69.26)	7.59 (7.78)	7.03 (7.02)	8.04 (8.21)
10a	158-159	64[d,e] (37)[e]	168.45	151.04	121.57	3255, 2940, 2900, 2845, 1630, 1598 (w), 1318, 1160, 1137, 1109, 1000.	$C_{24}H_{33}N_3O_4S_2$ (491.66)	58.63 (58.52)	6.77 (6.81)	8.55 (8.03)	13.04 (13.03)
10b	196-198	11[d,e]	168.44	150.44	123.57	3235, 3040, 3000, 2955, 2920, 2890, 1635, 1595 (w), 1315, 1140, 1008.	$C_{26}H_{37}N_3O_4S_2$ (519.72)	60.09 (60.20)	7.18 (7.78)	8.09 (8.02)	12.34 (12.33)
10c	130-131	75[e]	167.08	151.27	124.48	3255, 3045, 2950, 2915, 2855, 1640, 1598, 1315, 1160, 1141, 1109, 1020.	$C_{26}H_{37}N_3O_4S_2$ (519.72)	60.09 (60.03)	7.18 (8.07)	8.09 (8.02)	12.34 (12.34)

[a]Based on the ^{1}H NMR spectrum the product consists of an approx. 1:1 mixture of diastereomers of **8a** and besides 0.5 equiv. of **9a**. [b]4.5:1 mixture of diastereomers according to the ^{1}H NMR spectrum. [c]main diastereomer. [d]Catalyzed by boron trifluoride diethyl etherate (0.1 equiv.). [e]Yield based on **1**.

(EA/cyclohexane). - ^{1}H NMR ($CDCl_3$): δ (main diastereomer) = 0.60 (t, *J* = 7.0 Hz, 3 H, CH_3CH_2N), 1.12 (t, *J* = 7.3 Hz, 3 H, CH_3CH_2C-3), 1.73 (d, *J* = 7.1 Hz, 3 H, CH_3C-6), 2.61 (dq, *J* = 7.2 Hz, ^2J = 14.4 Hz, 1 H, HC*H*-C-3), 2.76 (dq, *J* = 7.3 Hz, ^2J = 14.5 Hz, 1 H, *H*CH-C-3), 3.11 (m, 1 H, HC*H*-N), 3.43 (m, 1 H, *H*CH-N), 4.42 (q, *J* = 7.1 Hz, 1 H, 6-*H*), 7.35-7.45, 7.85 (m, 10 H, aromatic H). - ^{13}C NMR ($CDCl_3$): δ (main diastereomer) = 10.02 (CH_3CH_2-C-3), 15.56 (CH_3CH_2N), 16.62 (CH_3-C-6), 28.13 (CH_2-C-3), 37.05 (CH_2N), 52.71 (HC-6), 87.13 (quart. *C*-3), 126.89, 127.73, 128.39, 128.57, 128.76, 131.04 (aromatic *C*H), 136.43, 138.01 (aromatic C).

N,N'-Diisopropyl-3,5-diphenyl-4-aza-2,4-heptadiene-2,6-disulfonamide (**10a**), obtained from 3.33 mmol **1c** (0.525 g), **7a** (0.83 g) in the presence of boron trifluoride diethyl etherate (47 mg, 0.33 mmol) at -78 °C: CC using PE/EA (5/1), yellow crystals (diethyl ether/PE). - ^{1}H NMR ($CDCl_3$): δ = 0.61 (d, *J* = 6.5 Hz, 3 H, CH_3CH-NH), 1.15 (d, *J* = 6.5 Hz, 3 H, CH_3CH-NH), 1.31 (d, *J* = 6.6 Hz, 3 H, CH_3CH-NH), 1.33 (d, *J* = 6.6 Hz, 3 H, CH_3CH-NH), 1.86 (d, *J* = 6.8 Hz, 3 H, CH_3CH-SO_2), 2.10 (s, 3 H, CH_3C=C), 3.45 [sept, *J* = 6.5 Hz, 1 H, $(CH_3)_2CH$], 3.51 [sept, *J* = 6.6 Hz, 1 H, $(CH_3)_2CH$], 4.34 (q, *J* = 6.8 Hz, 1 H, CH_3CH-SO_2), 5.76 (d, *J* = 6.5 Hz, 1 H, *H*N), 6.72, 6.94, 7.07, 7.28 (m, 11 H, aromatic H, *H*N). - ^{13}C NMR ($CDCl_3$): δ = 16.10 (CH_3CH-SO_2), 17.20 (CH_3C=C), 22.25, 22.65, 24.47, 24.53 (CH_3CH-NH), 46.09, 46.43 (CH-NH), 65.79 (CH-SO_2), 126.67, 127.70, 128.01, 128.15, 128.39, 130.50 (aromatic *C*H), 137.05, 138.82 (aromatic C).

N,N'-Di-tert.butyl-3,5-diphenyl-4-aza-2,4-heptadiene-2,6-disulfonamide (**10b**), obtained from 5 mmol **1d** (0.86 g), **7a** (1.4 g) in the presence of boron trifluoride diethyl etherate (71 mg, 0.5 mmol) at -78 °C: CC using PE/EA (5/1), yellow crystals (diethyl ether/PE). - ^{1}H NMR ($CDCl_3$): δ = 1.01 [s, 9 H, $(CH_3)_3$C], 1.42 [s, 9 H, $(CH_3)_3$C], 1.86 (d, *J* = 6.8 Hz, 3 H, CH_3CH), 2.08 (s, 3 H, CH_3C=C), 4.32 (q, *J* = 6.8 Hz, 1 H, CH_3CH), 5.80 (s, 1 H, *H*N), 6.70, 7.05, 7.27 (m, 11 H, aromatic H, *H*N). - ^{13}C NMR ($CDCl_3$): δ = 15.98 (CH_3CH), 16.24 (CH_3C=C), 29.80, 30.10 [$(CH_3)_3$C], 53.99, 54.98 (quart. *C*), 67.50 (CH), 126.77, 127.64, 127.90, 127.96, 128.35, 130.38 (aromatic *C*H), 137.44, 139.29 (aromatic C).

N,N'-Diisopropyl-4,6-diphenyl-5-aza-3,5-nonadiene-3,7-disulfonamide (**10c**), obtained from 1 mmol **1c** (0.158 g) and **7b** (0.277 g): without CC, yellow crystals (two recrystallizations from diethyl ether/PE). - ^{1}H NMR ($CDCl_3$): δ = 0.52 (d, *J* = 6.5 Hz, 3 H, CH_3CH), 1.01 (t, *J* = 7.4 Hz, 3 H, 9-H_3), 1.12 (d, *J* = 6.5 Hz, 3 H, CH_3CH), 1.21 (t, *J* = 7.4 Hz, 3 H, 1-H_3), 1.31 (d, *J* = 6.5 Hz, 3 H, CH_3CH), 1.35 (d, *J* = 6.5 Hz, 3 H, CH_3CH), 2.27 (dq, *J* = 7.4 Hz, ^2J = 14.6 Hz, 1 H, 2-*H*), 2.36 (m, 2 H, 8-H_2), 2.48 (dq, *J* = 7.2 Hz, ^2J = 14.4 Hz, 1 H, 2-*H*), 3.43 [sept, *J* = 6.5 Hz, 1 H, $(CH_3)_2CH$], 3.51 [sept, *J* = 6.5 Hz, 1 H, $(CH_3)_2CH$], 4.12 (dd, *J* = 4.2, 10.1 Hz, 1 H, 7-*H*), 5.72 (d, *J* = 6.2 Hz, 1 H, *H*N), 6.66 - 7.30 (several m, 11 H, aromatic H, *H*N). A ^{1}H,^{1}H-COSY experiment verified the assignment of specified peaks. - ^{13}C NMR ($CDCl_3$): δ = 11.92 (H_3C-9), 15.27 (H_3C-1), 22.29, 22.42 (CH_3CH), 24.03, 24.35 (H_2C-2,8), 24.52, 24.66 (CH_3CH), 45.93, 46.40 ($CHCH_3$), 72.68 (HC-7), 127.24, 127.49, 127.70, 128.23, 128.39, 130.63 (aromatic *C*H), 136.71, 139.26 (aromatic C).

***Trapping of N-Sulfonylamine* 2c, *generated from precursor* 5, *with 2-Aza-1,3-dienes* (7)**: To a stirred mixture of **5** and **7** (1 equiv.) in dichloromethane (2 ml/mmol **5**) triethylamine (1 equiv.) was added within 30 min at room temperature. The reaction was completed after stirring overnight. Then the mixture was diluted with dichloromethane (100 ml) and this solution washed twice with water (10 ml), dried ($MgSO_4$) and concentrated for CC. For yields, analytical and spectroscopic data of the isolated cycloadducts **8** see Table 1.

3-Ethyl-2-isopropyl-6-methyl-3,5-diphenyl-3,6-dihydro-2H-1,2,4-thiadiazine-1,1-dioxide (**8c**), obtained from 2.33 mmol **5** (0.625 g) and **7a** (0.581 g): CC using PE/EA (6/1), colorless crystals (EA/PE). - ^{1}H NMR

($CDCl_3$): δ = 0.97 (d, *J* = 6.8 Hz, 3 H, C*H*$_3$CH-N), 1.07 (t, *J* = 7.4 Hz, 3 H, C*H*$_3$CH$_2$), 1.50 (d, *J* = 6.8 Hz, 3 H, C*H*$_3$CH-N), 1.71 (d, *J* = 7.0 Hz, 3 H, C*H*$_3$C-6), 2.30 (dq, *J* = 7.3 Hz, ^2J = 14.6 Hz, 1 H, CH$_3$-HC*H*), 2.58 (dq, *J* = 7.3 Hz, ^2J = 14.6 Hz, 1 H, CH$_3$-*H*CH), 3.82 [sept, *J* = 6.8 Hz, 1 H, (CH$_3$)$_2$C*H*], 4.36 (q, *J* = 7.0 Hz, 1 H, 6-*H*), 7.36, 7.48, 7.88 (m, 10 H, aromatic H). - ^{13}C NMR ($CDCl_3$): δ = 9.55 (*C*H$_3$CH$_2$), 16.11 (*C*H$_3$C-6), 21.20, 23.02 (*C*H$_3$CH-N), 32.36 (*C*H$_2$), 49.96 (*C*H-N), 54.63 (H*C*-6), 87.13 (quart. *C*-3), 126.91, 127.51, 127.86, 128.00, 128.79, 131.09 (aromatic *C*H), 136.32, 138.05 (aromatic C).

6-Ethyl-2-isopropyl-3,5-diphenyl-3-propyl-3,6-dihydro-2H-1,2,4-thiadiazine-1,1-dioxide **8d** obtained from 2 mmol **5** (0.537 g) and **7b** (0.554 g): CC using PE/EA (6/1), colorless crystals (EA/PE). - ^{1}H NMR ($CDCl_3$): δ = 0.95 (d, *J* = 6.8 Hz, 3 H, C*H*$_3$CH), 0.98 (t, *J* = 7.5 Hz, 3 H, C*H*$_3$CH$_2$CH$_2$), 1.25 (t, *J* = 7.4 Hz, 3 H, C*H*$_3$CH$_2$C-6), 1.38 (m, 1 H, H$_3$C-*H*CH-CH$_2$), 1.50 (d, *J* = 6.8 Hz, 3 H, C*H*$_3$CH), 1.62 (m, 1 H, H$_3$C-HC*H*-CH$_2$), 1.89 (ddq, *J* = 3.82, 7.5 Hz, ^2J = 15.0 Hz, 1 H, H$_3$C-HC*H*-C-6), 2.13 (ddd, *J* = 4.7, 12.0 Hz, ^2J = 13.8 Hz , 1 H, CH$_3$CH$_2$-HC*H*), 2.26 (ddq, *J* = 7.4 Hz, ^2J = 14.9 Hz, 1 H, H$_3$C-*H*CH-C-6), 2.50 (ddd, *J* = 4.2, 11.8 Hz, ^2J = 13.6 Hz, 1 H, CH$_3$CH$_2$-*H*CH), 3.81 [sept, *J* = 6.8 Hz, 1 H, (CH$_3$)$_2$C*H*], 4.14 (dd, *J* = 3.8, 7.7 Hz, 1 H, 6-*H*), 7.32, 7.44, 7.82 (m, 10 H, aromatic H). A ^{1}H,^{1}H-COSY experiment verified the assignment of specified peaks. - ^{13}C NMR ($CDCl_3$): δ = 13.55, 14.42 (*C*H$_3$CH$_2$), 18.09 (CH$_3$*C*H$_2$CH$_2$), 21.09, 22.95 (*C*H$_3$CH), 25.26 (*C*H$_2$C-6), 41.85 (*C*H$_2$C-3), 49.99 (*C*H-N), 61.08 (H*C*-6), 86.66 (quart. *C*-3), 126.94, 127.39, 127.85, 127.95, 128.74, 131.00 (aromatic *C*H), 137.04, 138.36 (aromatic C).

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