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NOVEL GENERATION AND CYCLOADDITION REACTIVITY OF N-PHENYLSULFONYLBENZONITRILIMINE VIA THERMAL DECOMPOSITION OF N-(PHENYLSULFONYL)BENZOHYDRAZONOYL CHLORIDE

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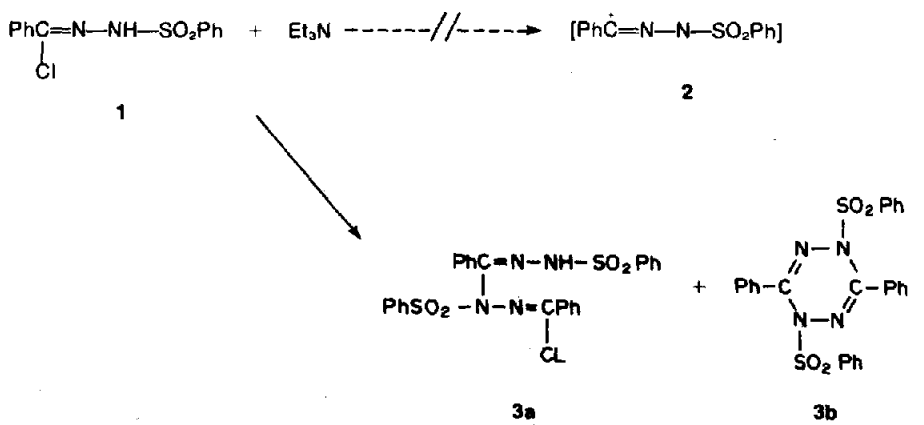
Abstract—Thermal decomposition of N(phenylsulfonyl)-benzohydrazonoyl chloride (**1**) in refluxing toluene generated N-phenylsulfonylbenzonitrilimine (**2**) which gave 1,3-dipolar cycloadducts with ethyl (**4a**) and methyl acrylate (**4b**), acrylonitrile (**4c**), styrene (**4d**), norbornene (**4e**), and norbornadiene (**4f**). The reactions with **4a–d**, **2** afforded regiospecifically 5-R substituted pyrazolines **5a–d** in lower yields. The reaction of **2** with **4e** gave only *exo* adduct **5e**, while the reaction with **4f** gave both *exo*- ($5f_x$) and *endo* adducts ($5f_n$) as well as their retro-Diels-Alder product **6**.

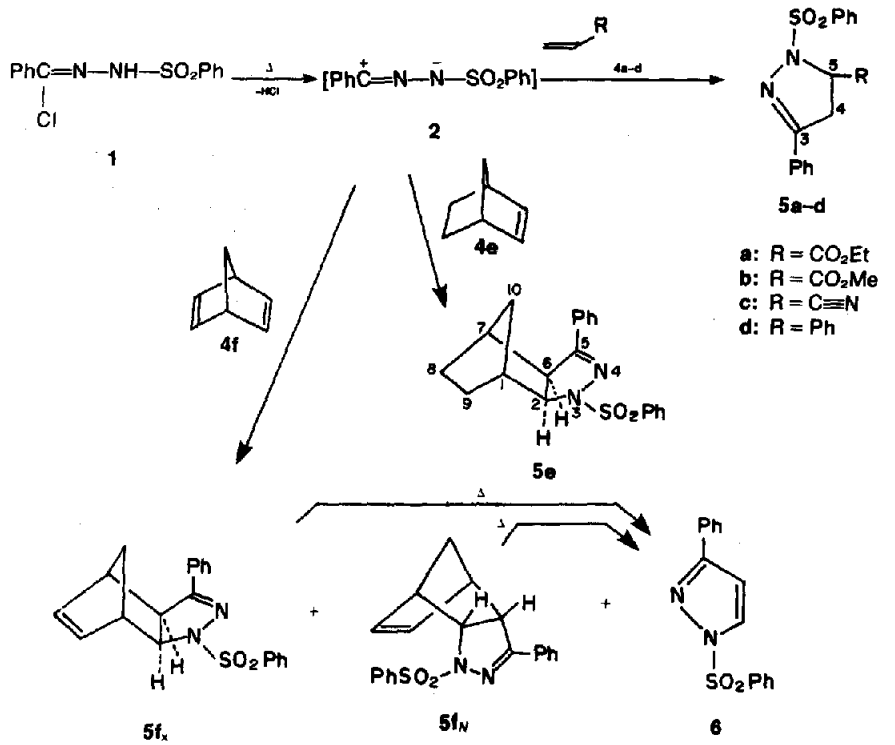
An N-(arylsulfonyl)benzohydrazonoyl chloride such as **1**, readily obtainable from the corresponding hydrazide and thionyl chloride,[1] has been shown recently to be a useful intermediate for synthesis of various azoles and azines.[2,3] However, attempted generation and cycloaddition of N-phenylsulfonylnitrilimine (**2**), a potentially useful 1,3-dipole for synthesis of N-phenylsulfonyl pyrazolines and pyrazoles,[4] from **1** *via* base-induced dehydrochlorination was not successful affording only a linear dimer **3a** and dihydrotetrazine **3b**, a cyclisation product of **3a**[1,2a,3a] (Scheme 1). Although N-*p*-tolylsulfonylnitrilimine has been suggested as a labile intermediate in the thermal decomposition of 2 - *p* - tolylsulfonyl - 5 - phenyltetrazole,[3a,5] there seems no report on the successful 1,3-dipolar cycloaddition of N-arylsulfonylnitrilimines.[6] On the other hand, thermal decomposition of hydroxamoyl chloride is known to be a unique method for generation of nitrile oxides which give 1,3-dipolar cycloadducts in good yields.[7] We have now found that thermal decomposition of the chloride **1** in inert solvent such as toluene provides a novel and facile method for generation of N-phenylsulfonylnitrilimine (**2**). This paper describes thermal generation of **2** and its 1,3-dipolar cycloaddition reactivity.

RESULTS AND DISCUSSION

The reaction of N-phenylsulfonylbenzohydrazonoyl chloride (**1**) and ethyl acrylate (**4a**) after work up and purification afforded 1 - phenylsulfonyl - 3 - phenyl - 5 - ethoxycarbonyl - Δ^2 - pyrazoline (**5a**), a 1,3-dipolar cycloadduct of **2** to **4a** in 11% yield. Similarly, reactions of **1** with methyl acrylate (**4b**), acrylonitrile (**4c**) and styrene (**4d**) gave the corresponding 1,3-dipolar cycloadducts **5b–d** in lower yields as summarised in Scheme 2 and Table 1. The assigned 5-R substituted structures **5a–d** were supported by analytical and spectral data (IR, ^{1}H NMR and ^{13}C NMR, Table 2 and 3). In ^{1}H NMR spectra, **5a–d** had characteristic signals due to H_4 and H_5 (Table 2).[8] In ^{13}C NMR spectra, **5a–d** revealed characteristic three lines assignable to C_3(s, δ 156.2–156.6), C_4



Scheme 1.



Scheme 2.

Table 1. Cycloadducts of nitrilimine 2 with olefins (4a–f)[a]

Olefin (mol ratio to 1)	React. time,hr	Product[b]	Yield,%	M.p.,°C(Solvent)[c,d]
4a(10)	10	5a	11.0	87-88 (MeOH)
4b(10)	28	5b	10.0	132-133(MeOH)
4c(10)	22	5c	7.0	188-189(EtOH)
4d(20)	20	5d	12.0	205-206(EtOH)
4e(10)	10	5e	53.0	199-200(EtOH)
4f(10)	10 (10)[e][4][f]	5fx	28.0 (29.0)[e][19.0][f]	173-174(EtOH)
		5fn	4.0 (4.0)[e][3.0][f]	156-157(EtOH)
		6	4.0 (4.0)[e][19.0][f]	91-92 (n-C_6H_{14}-C_6H_6)

[a] A mixture of 1 (2-3 mmol) and olefin was heated under reflux in toluene. [b] 5a-5fn are colorless prisms; 6 is colorless plates. [c] Solvent for recrystallization. [d] Many side products were also produced (see Experimental). [e] The reaction at 110° in chlorobenzene. [f] The reaction under reflux in chlorobenzene.

(t, δ 38.5–43.9) and C_5 (d, δ 49.0–65.2) respectively, supporting the given 2-phenyl-5-R substituted Δ^2-pyrazoline structures (Table 3).[9]

The reaction of 1 with norbornene (4e) afforded exclusively *exo*-adduct 5e in 53% yield, while the reaction with norbornadiene (4f) yielded *exo*- and *endo*-1:1 adducts, $5f_x$ and $5f_n$, and 1 - phenylsulfonyl - 3 - phenylpyrazole (6) in 28, 4 and 4% yields, respectively (Scheme 2 and Table 1). The stereochemistry of 5e, $5f_x$ and $5f_n$ was based on ^{1}H NMR spectra (Table 2). The coupling constants, $J_{1,2} = 4.1$ Hz and $J_{6,7} = 3.8$ Hz for $5f_n$ supported the given *endo*-adduct structure, while nearly zero values of $J_{1,2}$ and $J_{6,7}$ for 5e and $5f_x$ were compatible with the given *exo*-adduct structures.[10,11] ^{13}C NMR spectra of 5e, $5f_x$ and $5f_n$ had also characteristic pyrazoline ring carbons (Table 3). Compound 6 had characteristic ^{1}H NMR signals due to pyrazole ring protons (Table 2), and was a retro-Diels–Alder product of $5f_x$ and $5f_n$ as indicated by its formation from $5f_x$ and/or $5f_n$ on heating in refluxing toluene and also by the increased yield (19%) of 6 in the reaction of 1 with 4f at a higher reaction temperature (in refluxing chlorobenzene) (Table

Table 2. Analytical and Physical Data of Cycloadducts (5a–f) and 6

Compd	IR(KBr), cm^{-1}	^1H NMR Chemical shifts(ppm,δ) (60Mhz in $CDCl_3$, J in Hz)[a]	Analyses Formula	Found(Calcd)(%) C	H	N
5a	1365,1180(ν_{SO_2}), 1740($\nu_{C=O}$)	3.35(d,$J_{4,5}$=10.5,2H;H_4), 4.45(t,$J_{5,4}$=10.5,1H;H_5), 1.35(t,J=7.2, 3H;CH_2CH_3), 4.31(q,J=7.2,2H;CH_2CH_3), 7.3-8.1(m,10H;ArH)	$C_{18}H_{18}N_2O_4S$	60.18 (60.32)	5.10 (5.06)	7.90 (7.82)
5b	1360,1175(νSO_2), 1750(νC=O)	3.37(d,$J_{4,5}$=10.5,2H;H_4), 4.48(t,$J_{5,4}$=10.5,1H,H_5), 3.85(s,3H;OCH_3), 7.3-8.1(m,10H;ArH)	$C_{17}H_{16}N_2O_4S$	59.14 (59.29)	4.71 (4.68)	8.05 (8.13)
5c	1365,1175(νSO_2), 2245(νC≡N)	3.52(d,$J_{4,5}$=9.7,2H;H_4), 4.72(t,$J_{5,4}$=9.7,1H;H_5), 7.3-8.1(m,10H;ArH)	$C_{16}H_{13}N_3O_2S$	61.61 (61.72)	4.21 (4.21)	13.77 (13.50)
5d	1360,1175(νSO_2)	3.07(q,$J_{B,A}$=18.0,$J_{B,X}$=8.0,1H;$H_{4(B)}$), 3.55(q,$J_{A,B}$=18.0,$J_{A,X}$=10.8, 1H;$H_{4(A)}$), 4.95(q,$J_{X,A}$=10.8,$J_{X,B}$=8.0,1H;$H_{5(X)}$), 7.3-7.9(m,15H;ArH)	$C_{21}H_{18}N_2O_2S$	69.42 (69.59)	5.15 (5.01)	7.71 (7.73)
5e	1355,1175(νSO_2)	3.18(d,$J_{6,2}$=9.0,1H;H_6), 3.92(d,$J_{2,6}$=9.0;1H;H_2), 2.52(bs,1H;H_7), 2.80(bs,1H;H_1), 1.0-1.8(m,6H;H_{8-10}), 7.2-8.0(m,10H;ArH)	$C_{20}H_{20}N_2O_2S$	68.01 (68.16)	5.71 (5.72)	7.95 (7.95)
5f$_x$	1360,1170(νSO_2)	3.44(d,$J_{6,2}$=9.3,1H;H_6), 4.24(d,$J_{2,6}$=9.3,1H;H_2), 3.14(bs,1H;H_7), 3.43(bs,1H;H_1), 1.66(bs,2H;H_{10}), 6.22(bs,2H;$H_{8,9}$), 7.2-8.0(m,10H; ArH)	$C_{20}H_{18}N_2O_2S$	68.54 (68.55)	5.05 (5.18)	7.90 (7.99)
5f$_n$	1350,1170(νSO_2)	3.82(dd,$J_{6,7}$=3.8,$J_{6,2}$=9.8,1H;H_6), 4.63(dd,$J_{1,2}$=4.1,$J_{2,6}$=9.8,1H; H_2), 3.15-3.38(m,1H;H_7), 3.38-3.60(m,1H;H_1), 1.47-1.55(m,2H; H_{10}), 5.83(dd,$J_{8,9}$=3.0,J=4.3,1H;H_{8or9}), 6.16(dd,$J_{9,8}$=3.0,J=6.0, 1H;H_{9or8}), 7.2-8.0(m,10H;ArH)	$C_{20}H_{18}N_2O_2S$	68.60 (68.55)	5.33 (5.18)	7.98 (7.99)
6	1375,1190(νSO_2)	6.68(d,$J_{4,5}$=2.6,1H;H_4), 8.11(d,$J_{5,4}$=2.6,1H;H_5), 7.3-8.0(m,10H; ArH)	$C_{15}H_{12}N_2O_2S$	63.53 (63.36)	4.33 (4.25)	9.98 (9.85)

[a] bs = broad singlet.

Table 3. ^{13}C NMR Data of Cycloadducts (5a–f)[a,b]

Compd	C_3	C_4	C_5	Phenyl carbons	Other carbons
5a	156.2(s)	38.5(t)	62.0(d)	135.4(s), 133.6(d), 130.9(d), 130.1(s), 129.0(d), 128.6(d), 127.3(d), 127.0(d)	169.8(s, C=O), 62.2(t, -O$\underline{C}H_2$-), 14.1(q, -$\underline{C}H_3$)
5b	156.3(s)	38.5(t)	61.8(d)	135.3(s), 133.6(d), 130.9(d), 130.0(s), 129.0(d), 128.7(d), 127.0(d)	170.2(s, C=O), 53.1(q, -OCH_3)
5c	156.3(s)	39.2(t)	49.0(d)	134.5(s) 134.3(d), 131.5(d), 129.2(s), 129.0(d), 127.0(d)	116.2(s, C≡N)
5d	156.6(s)	43.9(t)	65.2(d)	140.7(s), 136.0(s), 133.2(d), 130.7(s), 128.8(d), 128.5(d), 128.2(d), 126.9(d)	

	C_5	C_6	C_2	C_1,C_7	C_8,C_9	C_{10}	Phenyl carbons
5e	158.9(s)	56.0(d)	69.1(d)	43.9(d) 40.3(d)	24.0(t) 28.3(t)	33.0(t)	136.4(s), 133.0(d), 130.6(s), 130.3(d), 128.9(d), 128.6(d) 128.3(d), 128.2(d), 127.2(d)
5f$_x$	157.4(s)	56.5(d)	70.0(d)	50.4(d) 46.1(d)	136.2(d) 140.0(d)	43.7(t)	136.5(s), 133.1(d), 130.5(s), 130.3(d), 128.9(d), 128.6(d), 128.1(d), 127.0(d)
5f$_n$	157.9(s)	55.9(d)	68.2(d)	49.0(d) 48.1(d)	134.0(d) 136.2(d)	45.9(t)	136.8(s), 133.0(d), 130.8(s), 130.2(d), 128.9(d), 128.6(d), 128.0(d), 127.0(d)

[a] All resonances in ppm downfield from internal Me_4Si in $CDCl_3$. [b] See the structural formula for numbering of the carbon atoms.

1).[12] On the other hand, no interconversion between $5f_x$ and $5f_n$ was observed under the reaction conditions (in refluxing toluene) and the observed *exo* : *endo* ratio 7.0 is very similar to 6.7 reported for the reaction of diphenylnitrilimine with **4f**.[13]

In order to examine the 1,3-dipolar cycloaddition reactivity of **2**, we examined also the reactions of **1** with cyclohexene, cycloocta-1,5-diene, diethyl fumarate, diethyl maleate, methyl cinnamate as well as alkynes such as dimethyl acetylenedicarboxylate, ethyl propiolate and phenylacetylene, but the corresponding cycloadducts could not be obtained and only complex mixtures were produced, from which diphenyl disulfide, phenyl thiobenzoate, phenyl thiobenzenesulfonate, 1,2 - dibenzoyl - 1 - phenylsulfonyl - hydrazine and benzoic acid were isolated as common decomposition products. These products were also produced in thermal decomposition of **1** in the absence of dipolarophiles (Experimental).

Thermal or photo decomposition of 2,5-disubstituted tetrazoles is a general method for generation of the corresponding nitrilimine,[14,15] and in the thermolysis of 2 - *p* - tolylsulfonyl - 5 - phenyltetrazole, Wawzonek and Kellen isolated several decomposition products similar to the above decomposition products.[3a] Therefore, our present results of thermolysis of **1** in the presence and/or in the absence of dipolarophiles could most reasonably be explained in terms of the thermal generation of N - phenylsulfonyl - benzonitrilimine (**2**) from **1** *via* dehydrochlorination.

The regiochemistry and reactivity of 1,3-dipolar cycloadditions are rationalised recently in terms of frontier orbital theory by Houk.[16] The observed regiospecific formation of 5-R substituted pyrazolines **5a–d** from R substituted olefins **4a–d** is the same trend reported for diphenylnitrilimine, a LUMO (= lowest unoccupied molecular orbital)-controlled type 1,3-dipole. The phenylsulfonyl group of **2** may lower the LUMO energy compared with formonitrilimine as N-phenyl substituent and **2** should be also a LUMO-controlled type 1,3-dipole. Therefore, the cycloaddition reactivity of **2** is lower toward electron-deficient dipolarophiles as was observed. However, the reactivity of **2** toward electron-rich dipolarophiles like norbornene (**4e**) is comparable with diphenylnitrilimine.

EXPERIMENTAL

Microanalyses were performed with a Perkin–Elmer 240 elementla analyzer. M.ps were determined with a Yanagimoto micromelting point apparatus (hot-stage type) and are uncorrected. IR spectra were obtained with a Jasco IRA-1 spectrometer. ^{1}H NMR spectra were recorded on a Jeol JNM-C-60HL spectrometer at 60 MHz, while ^{13}C NMR spectra were recorded on a Jeol JNM-FX 60 FT NMR instrument at 15.04 MHz. All NMR spectral peak positions are given in parts per million (δ) downfield from tetramethylsilane as an internal standard.

General procedure for 1,3-dipolar cycloaddition of N-phenylsulfonylbenzonitrilimine (**2**). A soln of (**1**) (2.00 mmol) and an appropriate dipolarophile (20.0 mmol) in dry toluene (15 ml) was heated under argon and under reflux. After heating for 10–28 hr, during which a slow evolution of HCl gas ceased, the solvent was removed under vacuum, and the residue was purified on a silica gel column to afford adducts **5a–f** and **6**. The results are summarised in Table 1–3.

3 - *Phenylsulfonyl* - 5 - *phenyl* - 3,4 - *diazatricyclo* - [5.2.1.$0^{2,6\text{-exo}}$]*deca* - 4 - *ene* (**5e**). A soln of **1** (590 mg, 2.00 mmol) and **4e** (1.89 g, 20.0 mmol) in dry toluene (15 ml) was heated as above for 10 hr. Removal of the solvent and excess **4e** under vacuum gave a residue (742 mg) which was purified on a silica gel column eluting with Et_2O–C_6H_6 (2:98) to afford the adduct **5e** as colorless prisms after recrystallisation from EtOH (372 mg, 53.0%).

Thermal decomposition of **1** *in the absence of dipolarophiles.* A soln of **1** (590 mg, 2.00 mmol) in dry toluene (15 ml) was heated as above for 15 hr. The cooled reaction was concentrated to *ca* 8 ml under vacuum and was allowed to stand overnight at room temp. The resulting crystals were filtered off and washed with toluene to afford 1,2 - *dibenzoyl* - 1 - *phenylsulfonylhydrazine* as prisms after recrystallisation from EtOH (130 mg, 36.0%); m.p. 201–202°; IR(K)Br) 3200, 1690, 1660. 1375 and 1180 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 11.58 (s, 1H, disappeared on shaking with D_2O) and 7.3–8.3 (m, 15H). (Found: C, 63.08; H, 4.51; N, 7.20. $C_{20}H_{16}N_2O_4S$ requires: C, 63.15; H, 4.24; N, 7.37%).

The combined filtrate and washings were evaporated to dryness under vacuum to afford an oily residue which was purified on a silica gel column eluting with n-hexane-C_6H_6-Et_2O system (9:1:0 ~ 1:1:0 ~ 0:1:0 ~ 0:98:2) to give the following known compounds: diphenyldisulfide (41 mg, 20.0%); S-phenyl thiobenzoate (115 mg, 29.0%), m.p. 56–57° (lit.,[17] 56°); S-phenyl benzenethiosulfonate (40 mg, 17.0%), m.p. 43–44° (lit.,[18] 45°); the chloride **1** (60 mg, 10.0% recovery); benzoic acid (71 mg, 32.3%).

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