

***N*-(Phenylsulfonyl)- and *N*-Methyl-*N*-(phenylsulfonyl)benzohydrazonoyl Azides. Thermally Induced Cyclization to Tetrazoles and Decomposition to Benzonitriles¹⁾**

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N-(Phenylsulfonyl)- and *N*-methyl-*N*-(phenylsulfonyl)benzohydrazonoyl azides, prepared from the corresponding hydrazonoyl chlorides and sodium azide, undergo the cyclization to 5-phenyl-1-(phenylsulfonylamino)-1*H*-tetrazoles together with the competitive decomposition to benzonitriles and the Curtius-type rearrangement leading to semicarbazides when heated in benzene under reflux. The tetrazole formation of hydrazonoyl azides may be characteristic of such hydrazonoyl azides as those carrying an *N*-sulfonyl substituent, the strong electron-withdrawing nature of which probably promotes the cyclization.

Imidoyl azides are well known, in general, to cyclize to tetrazoles which are more stable than the azides themselves in many cases.²⁾ However, according to Hergarty *et al.*,³⁾ *N*-arylbenzohydrazonoyl azides, a class of imidoyl azides, do not undergo this type of cyclization under a variety of conditions in spite of the fact that the corresponding tetrazoles have been obtained from hydrazidines on treatment with nitrous acid;⁴⁾ the hydrazonoyl azides give only semicarbazides *via* an acid-induced Curtius-type rearrangement.

In the course of our investigation of arylsulfonylhydrazine derivatives, we found that the title hydrazonoyl azides undergo the cyclization to 1,5-disubstituted tetrazoles along with the competitive decomposition to benzonitriles. In the present paper, these characteristic behavior of *N*-(phenylsulfonyl)- (1) and *N*-methyl-*N*-(phenylsulfonyl)benzohydrazonoyl azides (2) are described.

Results and Discussion

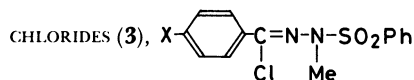
Preparation of *N*-Methyl-*N*-(phenylsulfonyl)benzohydrazonoyl Chlorides. *N*-Methyl-*N*-(phenylsulfonyl)benzohydrazonoyl chlorides (3b–f), the starting materials

for preparing hydrazonoyl azides 2, were obtained by the *N*-methylation of *N*-(phenylsulfonyl)benzohydrazonoyl chlorides (4)⁵⁾ with diazomethane according to the method previously reported for 3a.⁶⁾ The yields and physical data of 3b–f are listed in Table 1.

Preparation of *N*-(Phenylsulfonyl)- (1) and *N*-Methyl-*N*-(phenylsulfonyl)benzohydrazonoyl Azides (2).

Hydrazonoyl azides 1 and 2 were prepared by the reaction of the corresponding hydrazonoyl chlorides (4 and 3) with sodium azide. Azides 1 could be obtained in good yields by using aqueous dioxane as the solvent. The use of DMF or DMSO as the solvent caused the formation of considerable amounts of benzonitriles together with evolution of nitrogen even under cooling. On the other hand, azides 2 could be obtained in satisfactory yields when the reaction was carried out in DMSO at room temperature; and on treatment in aqueous dioxane, no formation of 2 was observed. The results are summarized in Scheme 1 and Table 2.

In the IR spectra of 2a–f, the azide ν_{as} band (near 2100 cm⁻¹) was observed to split into three peaks. ¹³C-NMR studies showed that compounds 2 exist in a single geometric isomer; thus, the ternary splits of azide

TABLE 1. PREPARATION OF *N*-METHYL-*N*-(PHENYLSULFONYL)BENZOHYDRAZONOYL

3	(X)	Yield ^{a)} %	Mp $\theta_m/^\circ\text{C}$ (Solvent) ^{b)}	IR (KBr)		NMR ^{c)} N-CH ₃ ^{d)}	Formula	Found (Calcd) (%)		
				$\nu_{C=N}$ cm ⁻¹	ν_{SO_2} cm ⁻¹			C	H	N
3b	(Me)	76	101–103 (B)	1592	1348 1165	3.03	C ₁₅ H ₁₅ N ₂ O ₂ SCl	55.97 (55.81)	4.76 (4.68)	8.46 (8.68)
3c	(OMe)	79	116–118 (B)	1603	1350 1175	3.00	C ₁₅ H ₁₅ N ₂ O ₃ SCl	53.38 (53.18)	4.52 (4.46)	8.08 (8.27)
3d	(Cl)	76	111–112 (B)	1579	1340 1153	3.06	C ₁₄ H ₁₂ N ₂ O ₂ SCl ₂	48.74 (48.99)	3.40 (3.52)	7.91 (8.16)
3e	(CN)	74	135–137 (T–H)	1593	1362 1173	3.14	C ₁₅ H ₁₂ N ₃ O ₂ SCl	53.98 (54.13)	3.62 (3.62)	12.59 (12.68)
3f	(NO ₂)	76	140–141 (T–H)	1579	1327 1155		C ₁₄ H ₁₂ N ₃ O ₄ SCl	47.73 (47.53)	3.40 (3.42)	11.96 (11.88)

a) Yield after recrystallization. b) Solvent for recrystallization; B: benzene, T–H: THF–hexane.

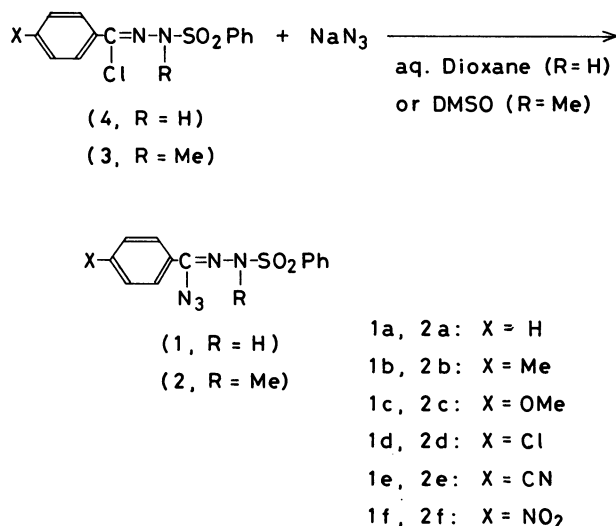
c) Data in CDCl₃ (δ) with TMS as an internal standard. Compound 3f is almost insoluble in CDCl₃.

d) Singlet.

TABLE 2. *N*-(PHENYLSULFONYL)-(1) AND *N*-METHYL-*N*-(PHENYLSULFONYL)BENZOHYDRAZONOYL AZIDES (2)

Azide	Yield/%	Mp (decomp) $\theta_m/^{\circ}\text{C}$	IR (KBr)/ cm^{-1}				NMR (CDCl_3) $\delta^{\text{b,c)}$			Found (Calcd) (%)		
			ν_{NH} cm^{-1}	assym. $\nu_{\text{N}_3^{\text{a)}}$ cm^{-1}	ν_{SO_2} cm^{-1}		N-H	N-CH ₃	Aromatic H	C	H	N
1a	90	118–120	3164	2130	1307 1160		8.29		7.40–8.23	C ₁₃ H ₁₁ N ₅ O ₂ S	51.64 3.64 23.35 (51.82 3.68 23.24)	
1b	84	117–118	3180	2140	1303 1165		8.17		7.04–8.20	C ₁₄ H ₁₃ N ₅ O ₂ S	53.07 4.09 22.45 (53.32 4.15 22.21)	
1c	93	131–132	3175	2150	1305 1165		8.11		6.78–8.20	C ₁₄ H ₁₃ N ₅ O ₃ S	50.74 3.97 21.35 (50.75 3.95 21.14)	
1d	93	142–143	3180	2145	1307 1170		8.33		7.36–8.26	C ₁₃ H ₁₀ N ₅ O ₂ SCl	46.61 2.99 20.56 (46.50 3.00 20.86)	
1e	80	133–134	3180	2140	1304 1168		8.39		7.40–8.64	C ₁₄ H ₁₀ N ₅ O ₂ S	51.42 2.98 26.00 (51.53 3.09 25.75)	
1f	86	140–141	3170	2160	1315 1167		8.29		7.35–8.50	C ₁₃ H ₁₀ N ₅ O ₄ S	44.97 3.01 24.01 (45.09 2.91 24.27)	
2a	93	77–78		2140 (2180, 2080)	1305 1158			2.93	7.25–8.15	C ₁₄ H ₁₃ N ₅ O ₂ S	53.37 4.14 22.45 (53.32 4.15 22.21)	
2b	95	100–102		2145 (2195, 2095)	1305 1178			2.91	7.00–8.16	C ₁₅ H ₁₅ N ₅ O ₂ S	54.76 4.58 20.98 (54.70 4.95 21.26)	
2c	91	110–112		2145 (2195, 2095)	1307 1160			2.91	6.70–8.15	C ₁₅ H ₁₅ N ₅ O ₃ S	52.30 4.35 19.97 (52.17 4.38 20.28)	
2d	96	120–121		2145 (2195, 2090)	1315 1165			2.72	7.21–8.32	C ₁₄ H ₁₂ N ₅ O ₂ SCl	48.00 3.46 19.98 (48.07 3.46 20.02)	
2e	94	100–102		2140 (2195, 2085)	1310 1174			3.04	7.28–8.15	C ₁₅ H ₁₂ N ₅ O ₂ S	53.18 3.57 24.29 (52.93 3.55 24.69)	
2f	96	115–116		2140 (2195, 2085)	1310 1168			3.29	7.15–8.53	C ₁₄ H ₁₂ N ₅ O ₄ S	46.65 3.30 23.04 (46.66 3.36 23.32)	

a) Minor peaks due to Fermi resonance are shown in parentheses. b) Signal patterns are as follows: N-H, broad siglet; N-CH₃, singlet; aromatic H, multiplet. c) Other signals are as follows: 1b, 2.40, s, *p*-CH₃; 1c, 3.86, s, *p*-OCH₃; 2b, 2.40, s, *p*-CH₃; 2c, 3.87, s, *p*-OCH₃.



Scheme 1.

ν_{as} band should be attributed to Fermi resonance. This type of Fermi resonance has been reported as regards some organic azides.⁷⁾

Azides **2** and azides **1** carrying an electron-donating group in the C-aryl group such as **1b** and **1c** are somewhat thermolabile, and **1e** and **1f** are comparatively stable.

Thermolyses of Hydrazoneyl Azides 1 and 2.

Hydrazoneyl azide **1a** was heated for 10h in dry benzene under reflux. Work-up gave 5-phenyl-1-(phenylsulfonylamino)-1*H*-tetrazole (**5a**, 14%), 4-phenyl-1-(phenylsulfonyl)semicarbazide (**6a**, 36%), and benzonitrile (**7a**, 28%). In Tables 3, 4, and 5, the results are summarized along with those obtained from **1b–f** which were treated under the same reaction conditions. In these reactions, small amounts of

TABLE 3. THERMOLYSES OF HYDRAZONOYL AZIDES (1 AND 2)

Azide	Products ^{a)} and yields/% ^{b,c)}		
	5 (8)	6 (9)	7
1a (2a)	14 (12)	36 (16)	28 (45)
1b (2b)	6 (6)	24 (23)	47 (48)
1c (2c)	— (—)	15 (15)	35 (31)
1d (2d)	13 (14)	29 (13)	56 (48)
1e (2e)	15 (16)	30 (10)	30 (64)
1f (2f)	13 (15)	34 (20)	23 (64)

a) The *p*-substituent of 5-aryl group of **5** (**8**), 4-aryl group of **6** (**9**), or compound **7** corresponds to that of C-aryl group of the respective reactant, **1a** (**2a**) to **1f** (**2f**). b) Data in parentheses are those of thermolyses of **2**. c) Isolated Yield except those of **7a** and **7b** which were detected by GLC.

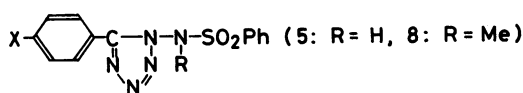
diphenyl disulfide and S-phenyl benzenethiosulfonate were also obtained.

On a similar treatment, hydrazoneyl azides **2** underwent the same type of reaction as those of **1** (Tables 3, 4, and 5). Methyl benzenesulfinate and benzenesulfonate were also detected besides S-phenyl benzenethiosulfonate in these cases.

The structure assignment of the tetrazoles and semicarbazides obtained was done on the basis of their analytical and spectral data, and the confirmation of the known compounds was made also by direct comparison with authentic specimens.

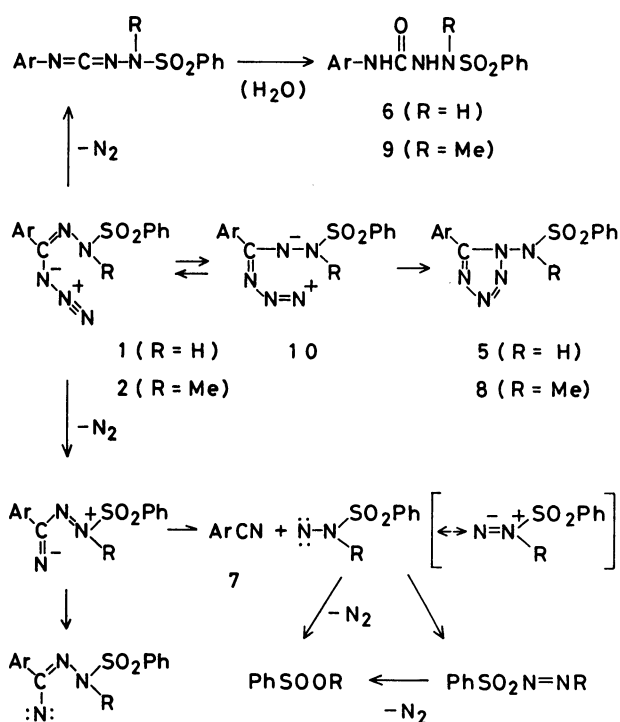
The present reactions can be explained by the following routes (Scheme 2).

S-Phenyl benzenethiosulfonate would be generated from benzenesulfinic acid *via* its disproportionation:⁸⁾ benzenesulfinic acid and methyl benzenesulfinate may be formed from the possible *N*-nitrene⁹⁾ or azo sulfone¹⁰⁾ intermediate (Scheme 2).

TABLE 4. PHYSICAL^{a)} AND ANALYTICAL DATA OF TETRAZOLES,

5 or 8	X	Mp $\theta_m/^\circ\text{C}$	IR (KBr)			Formula	Found (Calcd) (%)		
			ν_{NH} cm ⁻¹	ν_{SO_2} cm ⁻¹	$\nu_{\text{CN, ring}}$ cm ⁻¹		C	H	N
5a	H	179—180	3062	1362 1175	1265, 1087 983	C ₁₃ H ₁₁ N ₅ O ₂ S	51.83 (51.82)	3.68 (3.68)	23.19 (23.24)
5b	Me	188—189	3160	1357 1170	1275, 1085 995	C ₁₄ H ₁₃ N ₅ O ₂ S	53.65 (53.32)	4.26 (4.15)	22.11 (22.21)
5d	Cl	199—200	3190	1365 1170	1285, 1090 980	C ₁₃ H ₁₀ N ₅ O ₂ SCl	46.51 (46.50)	3.02 (3.00)	21.03 (20.86)
5e	CN	192—193	3200	1364 1170	1280, 1088 980	C ₁₄ H ₁₀ N ₆ O ₂ S	51.43 (51.53)	3.00 (3.09)	25.92 (25.75)
5f	NO ₂	206—207	3190	1365 1168	1280, 1085 995	C ₁₃ H ₁₀ N ₆ O ₄ S	45.19 (45.09)	2.90 (2.91)	24.04 (24.27)
8a	H	186—187		1378 1170	1272, 1088 977	C ₁₄ H ₁₃ N ₅ O ₂ S	53.41 (53.32)	4.20 (4.15)	22.48 (22.21)
8b	Me	174—175		1373 1168	1271, 1086 974	C ₁₅ H ₁₅ N ₅ O ₂ S	54.35 (54.70)	4.58 (4.59)	21.62 (21.26)
8d	Cl	173—175		1378 1168	1270, 1100 979	C ₁₄ H ₁₂ N ₅ O ₂ SCl	48.06 (48.07)	3.40 (3.46)	19.91 (20.02)
8e	CN	185—187		1375 1177	1275, 1095 1005	C ₁₅ H ₁₂ N ₆ O ₂ S	53.02 (52.94)	3.57 (3.55)	24.87 (24.70)
8f	NO ₂	199—202		1371 1167	1278, 1085 1000	C ₁₄ H ₁₂ N ₆ O ₄ S	46.64 (46.66)	3.30 (3.36)	23.38 (23.32)

a) NMR signals (CDCl₃/δ) of N-CH₃ in **8a**, **8b**, **8d**, and **8e** are 3.44, 3.41, 3.44, and 3.47 (singlet), respectively. Compound **8f** is almost insoluble in CDCl₃. Signals of N-H in compounds **5a**—**f** are comsealed by those of aromatic protons.



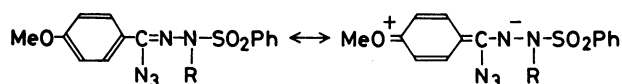
Scheme 2.

Since the disproportionation of benzenesulfonic acid gives also benzenesulfonic acid, the reaction medium should be acidic to a certain extent. Thus, the Curtius-

type rearrangement of **1** and **2** leading to **6** and **9** may be acid-induced. Indeed, when **1a** was heated in benzene in the presence of pyridine, **6a** was obtained in a diminished yield (3%) and an increase in the yield of **5a** was observed (14→40%). Methyl benzenesulfonate detected in the reaction of **2** may result from the ester interchange between methyl benzenesulfonate and benzenesulfonic acid.

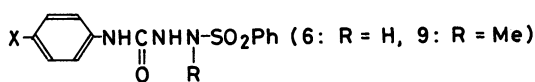
The tetrazole formation is one of the 1,5-dipolar cyclization. The present reaction is the first example of this type of cyclization of hydrazonoyl azides. The strong electron-withdrawing nature of benzenesulfonyl group probably accelerates the cyclization; that is, the 1,5-dipole structure, **10**, may be stabilized owing to the reduced electron density at the amino nitrogen. This type of contribution can not be expected for *N*-arylbenzohydrazonoyl azides which do not undergo tetrazole formation.

As shown in Table 3, hydrazonoyl azides **1c** and **2c** gave no tetrazoles, which can be explained on the basis of the electron-donating effect of *p*-methoxyl group attached to the C-aryl group. That is to say, the electron-donating group may prevent the transformation of azide forms (**1** and **2**) to the 1,5-dipole structure (**10**).



The lower yields of **5b** and **8b** may be also due to the electron-donating effect of *p*-methyl group.

TABLE 5. PHYSICAL AND ANALYTICAL DATA OF SEMICARBAZIDES.



6 or 9	X	Mp $\theta_m/^\circ\text{C}$	IR (KBr)			Formula	Found (Calcd) (%)		
			ν_{NH}	ν_{CO}	ν_{SO_2}		C	H	N
			cm^{-1}	cm^{-1}	cm^{-1}				
6a	H	204—206a)	3389, 3200 3100	1642	1347 1169	$\text{C}_{13}\text{H}_{13}\text{N}_3\text{O}_3\text{S}$	53.50 (53.60)	4.69 (4.50)	14.62 (14.42)
6b	Me	222—223	3409, 3202 3120	1649	1354 1176	$\text{C}_{14}\text{H}_{15}\text{N}_3\text{O}_3\text{S}$	55.10 (55.25)	4.98 (4.97)	13.90 (13.81)
6c	MeO	202—203	3400, 3200 3110	1644	1349 1171	$\text{C}_{14}\text{H}_{15}\text{N}_3\text{O}_4\text{S}$	52.30 (52.49)	4.73 (4.72)	13.10 (13.12)
6d	Cl	240—241	3316, 3275 3194	1674	1334 1164	$\text{C}_{13}\text{H}_{12}\text{N}_3\text{O}_3\text{SCl}$	47.87 (47.93)	3.70 (3.71)	12.85 (12.90)
6e	CN	234—236	3290, 3255 3190	1683	1325 1165	$\text{C}_{14}\text{H}_{12}\text{N}_4\text{O}_3\text{S}$	52.95 (53.16)	3.75 (3.82)	17.93 (17.71)
6f	NO_2	205—206	3311, 3247 3110	1692	1333 1161	$\text{C}_{13}\text{H}_{12}\text{N}_4\text{O}_5\text{S}$	46.21 (46.43)	3.54 (3.60)	16.72 (16.66)
9a	H	192—194	3302, 3210	1688	1349 1163	$\text{C}_{14}\text{H}_{15}\text{N}_3\text{O}_3\text{S}$	55.11 (55.07)	4.89 (4.95)	13.75 (13.76)
9b	Me	162—164	3361, 3097	1687	1360 1178	$\text{C}_{15}\text{H}_{17}\text{N}_3\text{O}_3\text{S}$	56.67 (56.41)	5.40 (5.36)	13.19 (13.16)
9c	MeO	188—189	3341, 3108	1697	1368 1177	$\text{C}_{15}\text{H}_{17}\text{N}_3\text{O}_4\text{S}$	53.58 (53.73)	5.42 (5.11)	12.23 (12.53)
9d	Cl	207—208	3305, 3092	1695	1355 1170	$\text{C}_{14}\text{H}_{14}\text{N}_3\text{O}_3\text{S}$	49.55 (49.49)	4.09 (4.15)	12.60 (12.37)
9e	CN	227—228	3323, 3280	1700	1360 1168	$\text{C}_{15}\text{H}_{14}\text{N}_4\text{O}_3\text{S}$	54.42 (54.54)	4.24 (4.27)	17.00 (16.96)
9f	NO_2	233—234	3307, 3097	1697	1330 1169	$\text{C}_{14}\text{H}_{14}\text{N}_4\text{O}_5\text{S}$	47.75 (48.00)	3.85 (4.03)	15.94 (15.99)

a) Lit, mp 228 $^\circ\text{C}$: P. Grammaticakis, *Bull. Soc. Chim. Fr.*, **1953**, 86.

Experimental

Melting points were determined with a Yanagimoto MP-S3 micromelting point apparatus, and are uncorrected. The microanalysis was performed on a Perkin-Elmer 240 elemental analyzer. The IR and NMR spectra were recorded with a Hitachi 260-10 and a Varian EM-360A spectrometer, respectively.

Preparation of N-Methyl-N-(phenylsulfonyl)benzohydrazonoyl Chlorides (3). *General Procedure:* To a solution of N-(phenylsulfonyl)benzohydrazonoyl chloride⁵ (4, 10 mmol) in THF (30 ml), slightly excess amounts of an ethereal solution of diazomethane was added by portions. The reaction completed almost immediately with evolution of nitrogen. The removal of solvent gave practically pure **3** (yield: nearly quantitative), which was recrystallized from an appropriate solvent. The results are summarized in Table 1.

Preparation of N-(Phenylsulfonyl)benzohydrazonoyl Azides (1). *General Procedure:* To a homogeneous aqueous dioxane solution of hydrazonoyl chloride **4**, prepared by adding water (10 ml) to a solution of **4** (10 mmol) in dioxane (40 ml), a solution of sodium azide (11 mmol) in water (5 ml) was added at room temperature. The mixture turned pale yellow immediately. After standing for a few minutes, 300 ml of ice water was added to the reaction mixture; and then, the mixture was ice-cooled for 10—15 min. The product separated was purified by crystallization from acetone-hexane. The results are summarized in Table 2.

Preparation of N-Methyl-N-(phenylsulfonyl)benzohydrazonoyl Azides (2). *General Procedure:* A mixture of hydrazonoyl

chloride **3** (10 mmol), sodium azide (12 mmol), and DMSO (60 ml) was stirred for 10—15 h at room temperature. To the reaction mixture, ice water was added by portions, and the resulting precipitates of hydrazonoyl azide were filtered, dried, and then crystallized from acetone-methanol. The results are summarized in Table 2.

Thermolyses of Hydrazonoyl Azides 1. Typical Procedure: A solution of **1a** (1.505 g, 5 mmol) in dry benzene (30 ml) was refluxed for 10 h. The progress of reaction was checked by means of TLC. The reaction mixture was cooled and filtered to give 4-phenyl-1-(phenylsulfonyl)semicarbazide (**6a**; 498 mg, 34%) as a benzene-insoluble substance, which was purified by crystallization from ethanol. The filtrate was concentrated to about 5 ml by fractional distillation, and then chromatographed on a silica-gel column (20 cm-d, 15 cm-h; eluents: hexane, benzene, benzene-diethyl ether, and benzene-ethanol) to give a benzonitrile fraction, diphenyl disulfide (22 mg, 2%), S-phenyl benzenethiosulfonate (203 mg, 16%), 5-phenyl-1-(phenylsulfonylamino)-1H-tetrazole (**5a**; 210 mg, 14%; purified by crystallization from ethanol-hexane), **6a** (29 mg, 2%), and an undeterminable mixture (202 mg). From the benzonitrile fraction, **7a** (144 mg, 28%) was detected by GLC (Silicone grease DC-550/celite 545, 2 m; 130 $^\circ\text{C}$). The results are summarized in Tables 3, 4, and 5.

Thermolysis of 1a in the Presence of Pyridine: A solution of **1a** (1.505 g, 5 mmol) and pyridine (0.4 g, 5 mmol) in dry benzene (30 ml) was refluxed for 10 h. A similar work-up of the reaction mixture gave **5a** (596 mg, 40%), **6a** (48 mg, 3%), and **7a** (171 mg, 33%) together with S-phenyl benzenethiosulfonate (132 mg, 11%) and trace amounts of diphenyl disulfide.

Thermolyses of Hydrazonoyl Azides 2. *Typical Procedure:* A solution of **2a** (1.575 g, 5 mmol) in dry benzene (30 ml) was refluxed for 3 h. The reaction mixture was treated in a manner similar to those mentioned above to afford **7a** (232 mg, 45%), **8a** (189 mg, 12%), and **9a** (245 mg, 16%) along with S-phenyl benzenethiosulfonate (62 mg), methyl benzenesulfinate (197 mg), methyl benzenesulfonate (141 mg), and an undeterminable mixture (73 mg). The results are summarized in Tables 3, 4, and 5.

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