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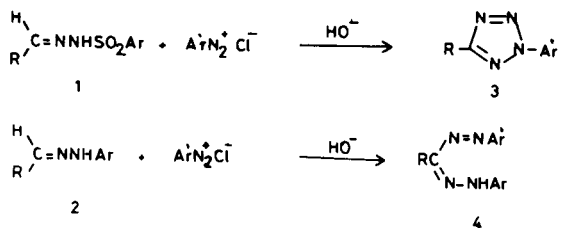
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A series of *N*- β -naphthalenesulfonylbenzohydrazidoyl chlorides **8a-d** has been prepared by the action of thionyl chloride on the corresponding hydrazides **7a-d**. Treatment of **8** with triethylamine and morpholine afforded the tetrazines **10** and the amidrazones **11** respectively. Acid hydrolysis of **11** yielded the hydrazides **7**. Reaction of **8** with phenylhydrazine gave 3,5-diaryltetrazoles **14**. However, reaction of **8** with aroylhydrazines yielded 3,5-diaryl-4- β -naphthalenesulfonylamino-4*H*-1,2,4-triazoles **15**. The structures of the products were assigned upon the basis of their spectra, elemental analyses and alternate synthesis wherever possible.

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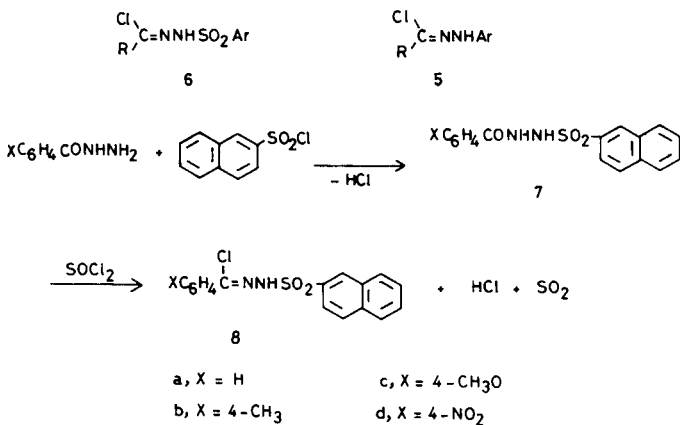
Introduction.

Literature reports indicate that aldehyde *N*-arenesulfonyl hydrazones **1** exhibit different behaviour from their *N*-aryl analogs **2**. For example, the reactions of **1** and **2** with arenediazonium salts in the presence of bases afforded 2,5-diaryltetrazoles **3** and the formazans **4** respectively (Scheme 1) [2-4]. The different behaviour of **1** was rationa-



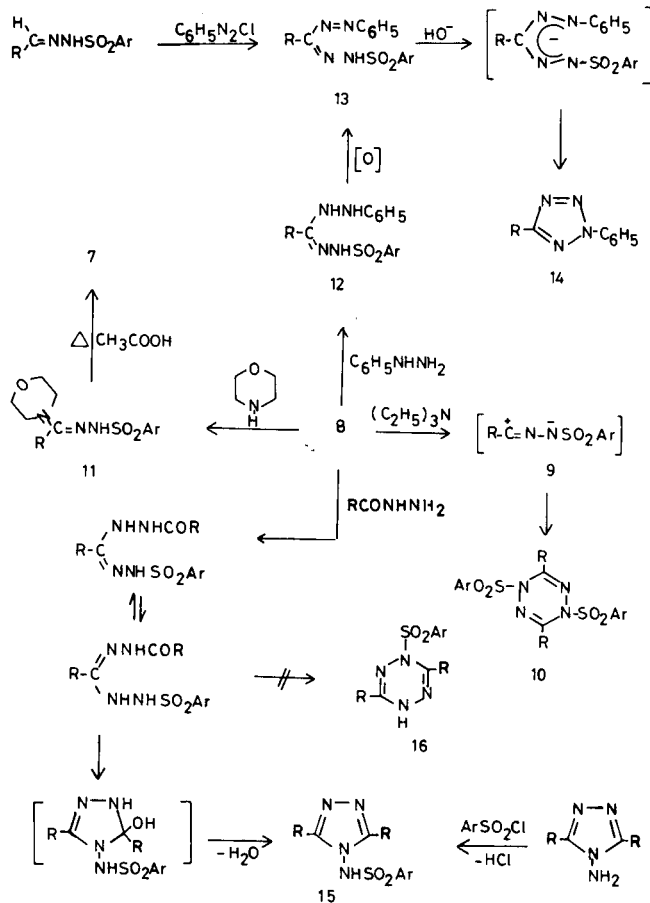
Scheme 1

lized in terms of the ease with which the arenesulfonyl group can be eliminated as arenesulfinate anion [2,3]. With this idea in mind and in continuation of our previous studies [5] directed towards exploring the synthetic potentialities of hydrazidoyl chlorides **5**, it was of interest to in-



Scheme 2

vestigate the reactions of *N*-arenesulfonylhydrazidoyl chlorides **6**. For this purpose, we have prepared a series of *N*- β -naphthalenesulfonylbenzohydrazidoyl chlorides **8a-d** from the corresponding hydrazides **7a-d** respectively (Scheme 2) and studied their reactions with some nitrogen



R = XC₆H₄ ; a, X = H b, X = 4-CH₃ c, X = 4-CH₃O d, X = 4-NO₂
Ar = 2-C₁₀H₇

Scheme 3

nucleophiles (Scheme 3). Both series of **7a-d** and **8a-d** have not yet been reported.

Results and Discussion.

The starting *N*-aroyl-*N'*- β -naphthalenesulfonylhydrazines **7a-d** were prepared by reacting aroylhydrazines with β -naphthalenesulfonyl chloride in pyridine (Scheme 1). Structural assignments for these hydrazides are based on their elemental and spectral analyses. The infrared spectra of these compounds were characterized by the presence of bands at 3370, 1675, 1600 and 1540 cm^{-1} assignable to NH, CO, C=C and amide II bands respectively. In addition they exhibit bands at 1350 and 1150 cm^{-1} assignable to sulfonyl group vibrations. The pmr spectra of **7a-d** were also compatible with their structures (see Experimental).

When the hydrazides **7a-d** were treated with thionyl chloride, the corresponding hydrazidoyl chlorides **8a-d** were obtained in 70-85% yields respectively. The structures of the latter chlorides were established by elemental analysis, molecular weight determination and by analysis of their spectra (ir and pmr) (see Experimental). The electronic absorption pattern was characterized in each case

by the presence of two intense ($\log \epsilon > 4$) bands in the regions 370-385 and 250-275 nm.

The reaction of **8a-d** with triethylamine was investigated as a method for the preparation of nitrile sulfonimides **9a-d**. Triethylamine in toluene converted **8a-d** into 1,4-dihydro-3,6-diaryl-1,4-bis(β -naphthalenesulfonyl)-s-tetrazines **10a-d** respectively. The formation of **10** confirms the intermediacy of **9**, which due to the lack of stabilizing factors, underwent dimerization to **10**. The tetrazine **10a** has also been isolated from the reaction of β -naphthalenesulfonyl chloride with phenyltetrazole in pyridine. By analogy to the reaction of *p*-toluenesulfonyl chloride with phenyltetrazole [6,7], the formation of **10a** can be ascribed to the dimerization of **9a**. The structures of the tetrazines **10a-d** were assigned on the basis of their spectra and elemental analysis data (see Experimental).

Secondary amines react with **8** to give the corresponding substitution products, however. Thus, when equivalent amounts of **8a** and morpholine were refluxed in ethanol, the amidrazone **11a** was obtained in almost quantitative yield. Similarly morpholinolysis of **8b-d** afforded the corresponding amidrazones **11b-d** respectively in 75-85% yields. Identification of these amidrazones was carried out by their analytical and spectral data and by their hydrolytic cleavage into the hydrazides **7a-d**. Thus, when **11a-d** were refluxed in acetic acid, they yielded the hydrazides **7a-d** respectively, which were identical in all respects with those prepared from β -naphthalenesulfonyl chloride and aroylhydrazines. The electronic absorption spectra of

Table I

Compound No.	Mp °C	Molecular Formula	Synthesized Compounds			
			Analysis %			
			C	H	N	S
8a	113	C ₁₇ H ₁₃ ClN ₂ SO ₂	59.22 (59.11)	3.80 (3.71)	8.12 (8.01)	9.28 (9.12)
8b	165	C ₁₈ H ₁₃ ClN ₂ SO ₂	60.25 (60.20)	5.84 (5.79)	7.80 (7.61)	8.93 (8.90)
8c	148	C ₁₈ H ₁₅ ClN ₂ SO ₃	57.67 (57.63)	4.03 (4.00)	7.47 (7.55)	8.55 (8.60)
8d	175	C ₁₇ H ₁₂ ClN ₂ SO ₄	52.38 (52.27)	3.10 (3.05)	10.78 (10.62)	8.22 (8.26)
10a	198	C ₃₄ H ₂₄ N ₄ S ₂ O ₄	66.22 (66.41)	3.92 (3.71)	9.08 (9.11)	10.37 (10.51)
10b	183	C ₃₆ H ₂₈ N ₄ S ₂ O ₄	67.06 (67.00)	4.37 (4.21)	8.69 (8.72)	9.94 (9.72)
10c	155	C ₃₆ H ₂₈ N ₄ S ₂ O ₆	63.89 (63.78)	4.17 (4.11)	8.28 (8.41)	9.47 (9.22)
10d	160	C ₃₄ H ₂₂ N ₆ S ₂ O ₈	57.78 (57.67)	3.14 (3.05)	11.89 (11.62)	9.07 (9.11)
11a	196	C ₂₁ H ₂₁ N ₃ SO ₃	63.78 (63.55)	5.35 (5.21)	10.62 (10.66)	8.10 (8.00)
11b	160	C ₂₂ H ₂₃ N ₃ SO ₃	64.52 (64.41)	5.66 (5.49)	10.26 (10.11)	7.82 (7.71)
11c	162	C ₂₂ H ₂₃ N ₃ SO ₄	62.09 (62.10)	5.45 (5.40)	9.87 (9.66)	7.53 (7.42)
11d	210	C ₂₁ H ₂₀ N ₄ SO ₃	57.26 (57.12)	4.57 (4.50)	12.72 (12.61)	7.28 (7.11)
15a	305	C ₂₄ H ₁₈ N ₄ SO ₂	67.59 (67.90)	3.42 (3.97)	13.13 (12.92)	7.51 (7.29)
15b	275	C ₂₆ H ₂₂ N ₄ SO ₂	68.70 (68.64)	4.87 (4.78)	12.33 (12.30)	7.05 (7.21)
15c	277	C ₂₆ H ₂₂ N ₄ SO ₄	64.18 (64.10)	4.55 (4.52)	11.51 (11.57)	6.59 (6.57)
15d	245	C ₂₄ H ₁₆ N ₆ SO ₆	55.81 (55.79)	3.12 (3.11)	16.27 (16.45)	6.20 (6.23)

Table II

The Spectral Data of Compounds Under Study

Compound No.	IR ν (cm^{-1}) [a]	NMR δ (ppm) [b]
8a	3195, 1605, 1350, 1160	6.9-8.8 (m)
8b	3190, 1612, 1350, 1165	2.78 (s, 3H), 7.0-8.8 (m, 12H)
8c	3200, 1610, 1350, 1135	3.80 (s, 3H), 6.8-8.9 (m, 12H)
8d	3200, 1605, 1350, 1130	7.0-8.0 (m)
10a	1605, 1310, 1180	7.0-8.7 (m)
10b	1605, 1350, 1180	2.3 (s, 6H), 7.0-8.8 (m, 22H)
10c	1605, 1350, 1180	3.81 (s, 6H), 6.9-8.5 (m, 22H)
10d	1600, 1390, 1185	6.9-8.5 (m)
11a	3340, 1610, 1320, 1150	3.0 (2d, 4H), 3.4 (2d, 4H), 6.9-8.5 (m, 13H)
11b	3335, 1605, 1330, 1155	2.3 (s, 3H), 3.1 (2d, 4H), 3.5 (2d, 4H), 6.8-8.4 (m, 12H)
11c	3335, 1605, 1330, 1155	3.8 (s, 3H), 3.0 (2d, 4H), 3.5 (2d, 4H), 6.8-8.8 (m, 12H)
11d	3340, 1610, 1335, 1150	3.1 (2d, 4H), 3.5 (2d, 4H), 6.8-8.7 (m, 12H)
15a	3120, 1605, 1360, 1160	7.5-8.7 (m)
15b	3110, 1607, 1350, 1160	2.4 (s, 3H), 2.5 (s, 3H), 7.6-8.4 (m, 16H)
15c	3110, 1608, 1355, 1170	3.82 (s, 3H), 3.85 (s, 3H), 7.6-8.6 (m, 16H)
15d	3115, 1608, 1355, 1170	7.3-8.9 (m)

[a] In potassium bromide. [b] In deuteriochloroform.

11a-d were similar to those of typical N^3,N^3 -disubstituted amidrazones [8]. For example, in ethanol they exhibit three intense bands ($\log \epsilon > 4$) in the regions 220-240, 245-270 and 330-350 nm.

Next the reaction of **8a-d** with phenylhydrazine was examined in an attempt to prepare the hydrazidines **12a-d** which can be oxidized to the formazan derivatives **13a-d** respectively. In our hands, treatment of **8a** with two equivalents of phenylhydrazine in tetrahydrofuran at room temperature and stirring the reaction mixture left, after the filtration of the precipitated phenylhydrazine hydrochloride, with potassium carbonate afforded 1,4-diphenyltetrazole **14a** (Scheme 3). The structure of the latter product **14a** was confirmed by its identity with an authentic sample prepared from coupling of benzaldehyde benzene-sulfonylhydrazone with benzene diazonium chloride in pyridine [2]. The hydrazidoyl chlorides **8b-d** react similarly with phenylhydrazine and give the corresponding 1,4-diaryltetrazoles **14b-d** respectively (Scheme 3). The sequence that may account for the formation of **14** and **8** and phenylhydrazine is outlined in Scheme 3.

When **8a** was refluxed with an equivalent amount of benzoylhydrazine in ethanol, 4- β -naphthalenesulfonylamino-4*H*-1,2,4-triazole **15a** was obtained in 80% yield. Other aroylhydrazines react similarly with **8** to give the corresponding 1,2,4-triazole derivatives **15b-d** respectively. Structural assignments for these products were based on their elemental and spectral analyses. For example, all compounds **15a-d** exhibit in their infrared spectra bands at 1605 (C=N), 1360, 1170 and 3120 cm^{-1} ($-\text{SO}_2\text{NH}-$). The structures of **15a-d** were also confirmed by the observation that all compounds dissolve in potassium hydroxide solution and precipitate upon acidification. Furthermore, the product **15a** was identical in all respects with an authentic sample prepared from 4-amino-3,5-diphenyl-4*H*-1,2,4-triazole [10] and β -naphthalenesulfonyl chloride in pyridine. This finding excludes further the isomeric tetrazine structure **16**. The probable mechanism that may account for the formation of **15** from **8** and aroylhydrazines is shown in Scheme 3.

EXPERIMENTAL

All melting points are uncorrected and were determined using a Thomas-Hoover melting point apparatus. The ir spectra (potassium bromide disc) were recorded on Perkin Elmer 257 grating spectrophotometer. The pmr spectra in deuterated chloroform were recorded on a Varian T60-A spectrometer using tetramethylsilane as the internal reference. The electronic absorption spectra were obtained in ethanol using Cary 17 spectrophotometer. Elemental analyses were performed by Galbraith Laboratory, Knoxville, Tennessee 37916, USA. Aroylhydrazines were prepared from the corresponding ethyl aroates and hydrazine hydrate in the usual way [11].

Preparation of **7a-d**.

β -Naphthalenesulfonyl chloride (11.3 g, 0.05 mole) was added portionwise to a solution of aroylhydrazine (0.05 mole) in pyridine (30 ml) with

stirring and external cooling. The reaction mixture was then allowed to come to room temperature and was poured with stirring into a mixture of hydrochloric acid (30%) and crushed ice. The solid that precipitated was collected, washed with dilute hydrochloric acid and finally with water. The product was purified by crystallization from acetic acid.

Compound **7a**.

This compound had mp 201°; ir (potassium bromide): 3270 (NH), 1670 (CO), 1600 (C=C), 1540 (amide II), 1340, 1170 (SO_2) cm^{-1} .

Anal. Calcd. for $\text{C}_{17}\text{H}_{14}\text{N}_2\text{SO}_3$: C, 62.57; H, 4.32; N, 8.58; S, 9.80. Found: C, 62.54; H, 4.21; N, 8.41; S, 9.87.

Compound **7b**.

This compound had mp 211°; ir (potassium bromide): 3320 (NH), 1675 (CO), 1600 (C=C), 1538 (amide II), 1340, 1155 (SO_2) cm^{-1} ; pmr (deuteriochloroform): δ 2.4 (s, 3H), 7.0-8.5 (m, 13H) ppm.

Anal. Calcd. for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{SO}_3$: C, 63.51; H, 4.73; N, 8.23. Found: C, 63.49; H, 4.69; N, 8.21.

Compound **7c**.

This compound had mp 192°; ir (potassium bromide): 3240 (NH), 1665 (CO), 1600 (C=C), 1535 (amide II), 1330, 1155 (SO_2) cm^{-1} ; pmr (deuteriochloroform): δ 3.80 (s, 3H), 6.7-8.6 (m, 13H) ppm.

Anal. Calcd. for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{SO}_3$: C, 60.66; H, 4.52; N, 7.86; S, 8.98. Found: C, 60.63; H, 4.51; N, 7.77; S, 8.91.

Compound **7d**.

This compound had mp 220°; ir (potassium bromide): 3275 (NH), 1666 (CO), 1600 (C=C), 1538 (amide II), 1340, 1160 (SO_2) cm^{-1} .

Anal. Calcd. for $\text{C}_{17}\text{H}_{14}\text{N}_2\text{SO}_3$: C, 54.98; H, 3.53; N, 11.35; S, 8.62. Found: C, 55.00; H, 3.51; N, 11.31; S, 8.92.

Preparation of **8a-d**.

To the appropriate 1-aroil-2- β -naphthalenesulfonylhydrazine **7** (0.03 mole) was added thionyl chloride (30 ml) and the mixture was refluxed for 3 hours (in case of **7d**, the period of reflux was 8 hours). The excess thionyl chloride was then distilled off under reduced pressure and the residue was triturated with petroleum ether (40/60°). The crude product that precipitated was collected and crystallized from benzene. The compounds obtained are listed in Table I together with their physical constants. Their infrared and pmr data are given in Table II.

Preparation of Tetrazines **10a-d**.

A solution of the appropriate hydrazidoyl chloride **8** (0.005 mole) in dry toluene (20 ml) was added to a vigorously stirred solution of triethylamine in the same solvent (80 ml) at 5-10° over a period of 1 hour. The resulting solution was stirred for 10 hours at room temperature and the precipitated triethylamine hydrochloride was filtered. Distillation of the solvent followed by addition of absolute ethanol (10 ml) to the residue gave the crude **10**. It was collected and crystallized from acetic acid. The tetrazines prepared by this method are listed in Table I and their characteristic spectral data are given in Table II.

Morpholinolysis of **8a-d**.

To a hot solution of the appropriate chloride **8** (0.001 mole) in ethanol (20 ml) was added morpholine (0.17 g, 0.002 mole). The mixture was refluxed for 30 minutes and then cooled. The crude amidrazone was collected and crystallized from ethanol. The amidrazones **11a-d** prepared are given in Table I and their spectral data are summarized in Table II.

Hydrolysis of Amidrazones **11a-d**.

A solution of the amidrazone **11a** (0.5 g) in acetic acid (90%, 20 ml) was refluxed for 30 minutes, left to cool and diluted with water. The solid that precipitated was collected and crystallization from acetic acid gave the hydrazide **7a** in 70% yield. Its melting point (201°) and mixed melting point with an authentic sample of **7a** showed no depression. When other amidrazones **11b-d** were similarly treated, they gave the hydrazides **7b-d** in 75-85% yields respectively.

Preparation of the Tetrazoles **14a-d**.

To a solution of **8a** (1.72 g, 0.005 mole) in tetrahydrofuran (15 ml) was added a solution of phenylhydrazine (0.01 mole) in the same solvent (15 ml) at room temperature. The reaction mixture was refluxed for 15 minutes and cooled. The precipitated phenylhydrazine hydrochloride was filtered and the filtrate was stirred with potassium carbonate (2.5 g) for 24 hours at room temperature. The mixture was filtered and the solvent was evaporated. The residue was triturated with water and the product was extracted with chloroform. Evaporation of the solvent and crystallization of the solid left from ethanol gave 2,5-diphenyltetrazole **14a** (50% yield), mp 101° (lit [11] mp 101-102°).

Other chlorides **8b-d** react similarly with phenylhydrazine and gave the tetrazoles **14b-d**.

Compound **14b**.

This compound had mp 95° (lit [12] mp 92-93°).

Compound **14c**.

This compound had mp 106-107° (lit [13] mp 105°).

Compound **14d**.

This compound had mp 202° (lit [14] mp 201-203°, lit [15] mp 199-200°).

Preparation of the Triazoles **15a-d**.

A mixture of equivalent amounts of the appropriate chloride **8** and arylhydrazine (0.002 mole each) in ethanol (20 ml) was refluxed for 6 hours. The white solid which precipitated was collected and crystallization from dimethylformamide-ethanol mixture gave the corresponding 4- β -naphthalenesulfonylamino-3,5-diaryl-4H-1,2,4-triazoles **15a-d** in 70-90% yields. The compounds prepared are listed in Table I together

with their physical constants and their spectral data are given in Table II. All products **15a-d** dissolve in aqueous potassium hydroxide solution and precipitate upon acidification. The product **15a** was identical in all respects with an authentic sample prepared from 3,5-diphenyl-4H-1,2,4-triazole and β -naphthalenesulfonyl chloride in pyridine.

REFERENCES AND NOTES

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