# Reactions with 1,8-Naphthosultam. Synthesis of [1,2]Benzisothiazolo[2,3,4-*cde*]benzotriazole 4,4-Dioxide. A New Ring System

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1,8-Naphthosultam (I) coupled with arenediazonium salts to give the 4-arylazo- VII, and the 2,4-bis-arylazo-1,8-naphthosultams, VIa-c. On the other hand, coupling of the 4-substituted 1,8-naphthosultams afforded the 2-phenylazo derivatives, IIa,b. Reduction of IIa,b gave the 2-amino compounds IVa,b, which reacted with nitrous acid to give the [1,2]benzisothiazolo[2,3,4-*cde*]benzotriazoles, Va,b, establishing thus a new ring system. The nitro analogue Vc was also synthesized.

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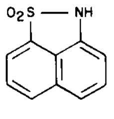
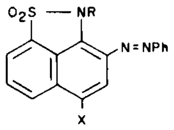
It is known that 1,8-naphthosultam (I) couples with arenediazonium salts to give 4-arylazo derivatives [1-3]. Now we have found that if the 4-position is occupied, coupling occurs at the 2-position to give the corresponding azo compounds. Thus, when the 4-substituted naphthosultams, namely, 4-chloro and 4-bromo-1,8-naphthosultams [4] were treated with benzenediazonium chloride in ethanol, in presence of sodium acetate, the corresponding 2-phenylazo derivatives IIa,b were obtained.



I



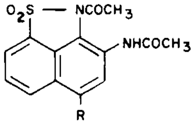
| II | R | X |
|---|---|---|
| a | H | Cl |
| b | H | Br |
| c | $CH_3$ | Br |

II

The ir spectrum of IIa displayed absorption band at 3230 $cm^{-1}$ (NH).

Methylation of IIb with dimethyl sulfate afforded the *N*-methyl derivative IIc. The ir spectrum of IIc showed no absorption at the NH region.

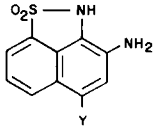
On reductive acetylation, the monoazo derivative IIb, gave *N*-acetyl-2-acetylamino-4-bromo-1,8-naphthosultam (IIIa). The ir spectrum of IIIa had absorption bands at 3250 $cm^{-1}$ (NH) and 1685 (CO).



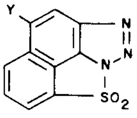
| III | R |
|---|---|
| a | Br |
| b | $NO_2$ |

III

When the monoazo derivatives, IIa,b, were reduced with zinc dust in acetic acid, and the amino compounds obtained, IVa,b, were treated with sodium nitrite and hydrochloric acid under cooling, the corresponding [1,2]benzisothiazolo[2,3,4-*cde*]benzotriazoles Va,b, with a new ring system, were obtained. The ir spectrum of Va showed no bands at the NH region while its pmr spectrum (DMSO-$d_6$) displayed signals at $\delta$ 7.82 ppm (s, 1H, Ar-H) and $\delta$ 8.14 ppm (m, 3H, Ar-H).



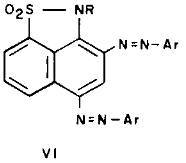
| IV, V | Y |
|---|---|
| a | Cl |
| b | Br |
| c | $NO_2$ |



IV V

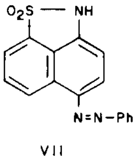
The nitro analogue Vc was prepared by treatment of the 2-amino-4-nitro-1,8-naphthosultam (IVc) with nitrous acid. Compound IVc could be synthesized by partial reduction of 2,4-dinitro-1,8-naphthosultam [5,6] with ammonium hydrogen sulfide. The ir and pmr spectra of IVc are in accordance with its structure. Its diacetyl derivative IIIb was also obtained and identified. The ir spectrum of IIIb showed absorption bands at 3150 $cm^{-1}$ (NH) and 1690 (C=O).

Coupling of I with two moles of arenediazonium salts in pyridine gave the corresponding 2,4-bis-arylazo compounds VIa-c. These bis-arylazo compounds are deeply coloured compounds, different from the corresponding monoarylazo compounds VII, prepared by coupling of I with benzenediazonium chloride in ethanol in presence of sodium acetate. The uv spectrum of VIa showed two maxima at 345 mμ ($\epsilon$ = 1.75 × $10^4$) and 410 mμ ($\epsilon$ = 1.6 × $10^4$) while that of VII showed two maxima at 240 mμ ($\epsilon$ = 1.9 × $10^4$) and 385 mμ ($\epsilon$ = 2.2 × $10^4$). The ir spectra of



VI

| VI | R | Ar |
|---|---|---|
| a | H | $C_6H_5$ |
| b | H | $C_6H_4CH_3$-p |
| c | H | $C_6H_4NO_2$-p |
| d | $CH_3$ | $C_6H_5$ |
| e | $CH_3$ | $C_6H_4CH_3$-p |
| f | $CH_3$ | $C_6H_4NO_2$-p |



VII

VIa,c showed absorption bands at 3400 and 3420 cm$^{-1}$, respectively (NH).

Methylation of VIa-c with dimethyl sulfate in presence of alkali yielded the corresponding *N*-methyl derivatives, VId-f. The ir spectra of VId-f showed no absorption bands at the NH region.

## EXPERIMENTAL

Melting points are uncorrected. The ir spectra were recorded (potassium bromide) with a Pye-Unicam SP 1000 spectrophotometer. The uv spectra were taken in dioxane with a Perkin-Elmer spectrophotometer model 402. The nmr spectra were taken in DMSO-d$_6$ with a Varian EM-390 NMR Spectrometer using TMS.

### 4-Chloro and 4-Bromo-2-phenylazo-1,8-naphthosultams (IIa,b).

A cooled solution of 4-chloro- or 4-bromo-1,8-naphthosultam (5 mmoles) in 50 ml of ethanol containing 3 g of sodium acetate was treated with a solution of benzenediazonium chloride (prepared from 5 mmoles of aniline hydrochloride) and left overnight. The reaction mixture was then poured into water. The products were collected, washed with water and crystallized from acetic acid.

Compound IIa was obtained as brown crystals, mp 280°, yield 76%; ir: 3240 cm$^{-1}$ (NH), 1340 ($\nu$ as SO$_2$) and 1160 ($\nu$ s SO$_2$).

*Anal.* Calcd. for $C_{16}H_{10}ClN_3O_2S$: C, 55.9; H, 2.9; N, 12.2; S, 9.3. Found: C, 55.6; H, 3.2; N, 12.0; S, 9.2.

Compound IIb was obtained as brown crystals, mp 238°, yield 70%.

*Anal.* Calcd. for $C_{16}H_{10}BrN_3O_2S$: C, 49.5; H, 2.6; N, 10.8; S, 8.3. Found: C, 49.3; H, 2.5; N, 11.1; S, 8.2.

### Methylation of 4-Bromo-2-phenylazo-1,8-naphthosultam (IIb).

A solution of 0.5 g of IIb in 100 ml of 3% aqueous sodium hydroxide was heated to 80° and treated gradually with 2 ml of dimethyl sulfate with vigorous shaking. The precipitate (IIc) that separated was filtered off, washed thoroughly with water and crystallized from acetic acid, mp 250°, yield 60%; ir: 1340 and 1160 cm$^{-1}$ (SO$_2$).

*Anal.* Calcd. for $C_{17}H_{12}BrN_3O_2S$: C, 50.8; H, 3.0; N, 10.5; S, 8.0. Found: C, 51.0; H, 3.1; N, 10.7; S, 7.8.

### *N*-Acetyl-2-acetylamino-4-bromo-1,8-naphthosultam (IIIa).

To a boiling mixture of 1 g of IIb, 10 ml of acetic acid and 10 ml of acetic anhydride was gradually added 1 g of zinc dust. The mixture was refluxed for 30 minutes and then filtered into 100 ml of ice-water. The solid that separated was collected and crystallized from ethanol, mp 252°; ir: 3250 cm$^{-1}$ (NH), 1685 (C=O), 1345 and 1160 (SO$_2$).

*Anal.* Calcd. for $C_{14}H_{11}BrN_2O_4S$: C, 43.9; H, 2.9; N, 7.3; S, 8.4. Found: C, 43.7; H, 2.8; N, 7.2; S, 8.6.

### [1,2]Benzisothiazolo[2,3,4-*cde*]benzotriazole 4,4-Dioxides (Va,b).

A solution of 2 g of IIa or IIb in 50 ml of acetic acid was heated to reflux, then 2 g of zinc dust were gradually added. After the colour of the solution had disappeared, the reaction mixture was filtered into an excess of cold water. The amino compounds, IVa or IVb, that precipitated was filtered off as rapidly as possible, then it was added to about 10 ml of concentrated hydrochloric acid, cooled in an ice bath and gradually treated with 0.5 g of sodium nitrite. The solid, Va or Vb, that formed was collected and crystallized.

Compound Va had mp 174° (explosion) from aqueous dioxane; ir: 1320, 1170 cm$^{-1}$ (SO$_2$), and 2150; pmr: $\delta$ 7.82 ppm (s, aromatic, 1H), 8.14 (m, aromatic, 3H).

*Anal.* Calcd. for $C_{10}H_4ClN_3O_2S$: C, 45.2; H, 1.5; N, 15.8; S, 12.1. Found: C, 45.0; H, 1.8; N, 15.6; S, 12.1.

Compound Vb had mp 180° (explosion) from dioxane; ir: 1320, 1160 (SO$_2$), 2150 cm$^{-1}$.

*Anal.* Calcd. for $C_{10}H_4BrN_3O_2S$: C, 38.7; H, 1.3; N, 13.6; S, 10.3. Found: C, 38.6; H, 1.2; N, 13.8; S, 10.3.

### 2-Amino-4-nitro-1,8-naphthosultam (IVc).

Hydrogen sulfide gas was passed through a solution of 1.5 g of 2,4-dinitro-1,8-naphthosultam in 50 ml of ethanol and 50 ml of ammonium hydroxide (21%). A yellow precipitate at first appeared and the gas was passed until a clear solution was obtained. The solution was acidified with hydrochloric acid and the orange crystals of IVc were filtered off, dried and recrystallized from dimethylformamide, mp 274° dec; yield 71%; ir: 3230 cm$^{-1}$ (NH), 1620 (NH$_2$), 1560 (NO$_2$), 1340 (NO$_2$ and SO$_2$), 1160 (SO$_2$); pmr: $\delta$ 6.9 ppm (broad, NH$_2$, 2H), 7.7 (m, aromatic, 2H), 8.6 (m, aromatic, 1H), 8.9 (s, aromatic, 1H).

*Anal.* Calcd. for $C_{10}H_7N_3O_4S$: C, 45.3; H, 2.7; N, 15.8; S, 12.1. Found: C, 45.6; H, 2.8; N, 15.6; S, 12.3.

### *N*-Acetyl-2-acetylamino-4-nitro-1,8-naphthosultam (IIIb).

A mixture of 0.5 g of IVc, 5 ml of acetic acid and 5 ml of acetic anhydride was refluxed for 1 hour, cooled and poured into 50 ml of ice-water. The solid, IIIb, that separated was collected, washed with water and crystallized from acetic acid, mp 245°; ir: 3150 cm$^{-1}$ (NH), 1690 (C=O), 1550 (NO$_2$), 1340 (NO$_2$ and SO$_2$), 1160 (SO$_2$).

*Anal.* Calcd. for $C_{14}H_{11}N_3O_6S$: C, 48.1; H, 3.2; N, 12.0; S, 9.2. Found: C, 47.9; H, 3.3; N, 11.9; S, 9.4.

### 8-Nitro[1,2]benzisothiazolo[2,3,4-*cde*]benzotriazole 4,4-Dioxide (Vc).

The amine IVc (1 g) was suspended in 20 ml of cold concentrated hydrochloric acid and gradually treated, while cooling with 0.5 g of sodium nitrite. The yellowish red product that precipitated was collected and crystallized from dioxane to give Vc, mp 170° (explosion).

*Anal.* Calcd. for $C_{10}H_4N_4O_4S$: C, 43.5; H, 1.5; N, 20.3; S, 11.6. Found: C, 43.3; H, 1.6; N, 20.0; S, 11.8.

### 2,4-Bis-arylazo-1,8-naphthosultams (VIa-c).

A solution of 1 g of I in 40 ml of pyridine was cooled in an ice-salt bath and gradually treated with 2 moles of the diazotized aniline. The reaction mixture was chilled for 24 hours, then poured into cold water and acidified with dilute hydrochloric acid. The solid that separated was filtered off and thoroughly washed with water.

Compound VIa was recrystallized from nitrobenzene in dark coloured crystals, mp 270°, yield 82%; ir: 3400 cm$^{-1}$ (NH), 1330 and 1190 (SO$_2$); uv: 345 m$\mu$ ($\epsilon$ = 1.75 × 10$^4$), 410 m$\mu$ ($\epsilon$ = 1.6 × 10$^4$).

*Anal.* Calcd. for $C_{22}H_{15}N_5O_2S$: C, 63.9; H, 3.7; N, 16.9; S, 7.8. Found: C, 63.7; H, 3.5; N, 17.1; S, 7.7.

Similarly, the 2,4-bis-*p*-tolyl- (VIb) and 2,4-bis-*p*-nitrophenylazo-1,8-naphthosultam (VIc) were obtained and they were identified as their *N*-methyl derivatives, VIe,f.

### *N*-Methyl-2,4-bis-arylazo-1,8-naphthosultams (VId-f).

One gram of each of VIa-c was dissolved in 100 ml of 5% aqueous sodium hydroxide and gradually treated with 0.5 ml of dimethyl sulfate. The solid that separated was filtered off and washed with water.

Compound VId was recrystallized from acetic acid, mp 240°, yield 73%; ir: 1335 and 1190 cm$^{-1}$ (SO$_2$).

*Anal.* Calcd. for $C_{23}H_{17}N_5O_2S$: C, 64.6; H, 4.0; N, 16.4; S, 7.5. Found: C, 64.4; H, 4.2; N, 16.4; S, 7.3.

Compound VIe was recrystallized from acetic acid, mp 265°, yield 71%; ir: 1335 and 1190 cm$^{-1}$ (SO$_2$).

*Anal.* Calcd. for $C_{25}H_{21}N_5O_2S$: C, 65.9; H, 4.6; N, 15.4; S, 7.0. Found: C, 66.2; H, 4.4; N, 15.2; S, 7.2.

Compound VIf was recrystallized from nitrobenzene, mp 285°, yield, 65%; ir: 1330 and 1190 cm$^{-1}$ (SO$_2$).

*Anal.* Calcd. for $C_{23}H_{15}N_7O_6S$: C, 53.4; H, 2.9; N, 18.9; S, 6.2. Found: C, 53.1; H, 2.8; N, 18.7; S, 6.0.

### 4-Phenylazo-1,8-naphthosultam (VII).

Compound I (1 g) was dissolved in 40 ml of ethanol containing 1.5 g of sodium acetate. The solution was cooled and treated with a solution of benzenediazonium chloride (from 0.65 g of aniline hydrochloride). The reaction mixture was then poured into cold water and the product was filtered off and crystallized from aqueous dioxane, mp 215°, yield 82%; ir: 3000 cm$^{-1}$ (broad, hydrogen bond, NH), 1330 and 1170 ($SO_2$); uv: 240 m$\mu$ ($\epsilon$ = 1.9 × 10$^4$), 385 m$\mu$ ($\epsilon$ = 2.2 × 10$^4$).

*Anal.* Calcd. for $C_{16}H_{11}N_3O_2S$: C, 62.1; H, 3.6; N, 13.6; S, 10.4. Found: C, 61.9; H, 3.7; N, 13.8; S, 10.6.

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