Nitration Studies of Naphtho[2,3-*c*][1,2,5]thiadiazole

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Nitration of naphtho[2,3-*c*][1,2,5]thiadiazole gives the 5-nitro derivative in 61-66% yield. Chlorination of this product apparently gives an unstable addition product which loses hydrogen chloride on recrystallization to give 4-chloro-8-nitronaphtho[2,3-*c*][1,2,5]thiadiazole. Thus, naphtho[2,3-*c*][1,2,5]thiadiazole under nitrating conditions behaves as a 2-substituted naphthalene rather than as an anthracene analog.

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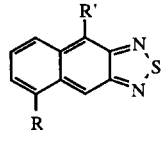
In a previous report in which the halogenation of naphtho[2,3-*c*][1,2,5]thiadiazole (**I**), a heterocyclic analog of anthracene, was investigated, it was found that the bromination and chlorination of **I** paralleled the behavior of anthracene. That is, the halogens added to **I** to give the 4,9-dihalo-4,9-dihydro derivatives as stable products. In the case of anthracene, the 9,10-dihalo adducts were unstable and underwent further change to produce the 9-haloanthracene.

Since treatment of anthracene with various nitrating agents appears to follow a path similar to that of halogenation [1], the behavior of **I** towards various nitrating agents was investigated.

In contrast to the behavior of anthracene, the nitration of **I** with nitric acid-sulfuric acid produced the 5-nitro derivative **II** in 61-66% yield.



I R = R' = H
II R = NO_2, R' = H
III R = NO_2, R' = Cl

The nitro compound could be smoothly reduced over palladium-charcoal catalyst to the corresponding amine in 66% yield. Reduction of the amine also occurred with ammonium sulfide solution.

In the halogenation of anthracene derivatives it has been suggested that *alpha* substituents make the addition compound more stable [2]. In the chlorination of **II**, a white solid which is presumably the addition product, was formed. This substance on workup, however, was converted to the orange chloronitro derivative **III** in 78% yield.

It appears that the addition compound readily loses hydrogen chloride to give the substitution product **III**. The selectivity with which one of the chlorines is lost can be attributed to the steric effect of the nearby nitro group.

By analogy to anthracene, which is nitrated in the 9-position, we would have expected that **I** would have been nitrated in the 4-position (the corresponding position of naphtho[2,3-*c*][1,2,5]thiadiazole). In the naphthalene series, a *meta*-directing group in one ring causes an entering substituent to go into the other ring. Thus, bromination of 2-nitronaphthalene gives the 5-bromo derivative. It appears that **I** behaves as though it were a naphthalene derivative rather than as an analog of anthracene. If we consider **I** as a naphthalene with an "NS" substituent in the 2-position, then the results are what one would expect if the substituent is a *meta*-directing group. Since the nitrations studied are done in acid medium, the nitrogen at the 2-position would be protonated under the conditions of the reaction and would be a *meta*-directing group.

EXPERIMENTAL

Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Infrared spectra (ir) were obtained on a Beckman IR-8 spectrophotometer and ultraviolet spectra (uv) on a Perkin-Elmer Model 202 spectrophotometer. Nuclear magnetic resonance spectra (nmr) were determined on a Varian HA-60-IL spectrometer with a C-1024 time-averaging computer using tetramethylsilane as internal standard. Gas chromatographic analyses were determined using a 20% SE-30-chromosorb P column. Elemental analyses were determined on an F and M Model 185 C,H,N-Analyzer by Mr. Daryl Sharp.

N-Sulfinylaniline was prepared according to the method of Pesin *et al.* [3] in 45-66% yield.

Naphtho[2,3-*c*][1,2,5]thiadiazole was prepared according to the method of Cava and Schlessinger [4] in 12-61% yield, mp 97-99°.

5-Nitro[2,3-*c*][1,2,5]thiadiazole.

Method A.

To an ice-cooled solution of naphtho[2,3-*c*][1,2,5]thiadiazole (0.50 g, 2.7 mmoles) in 10 ml of concentrated sulfuric acid was added a mixture of 0.2 ml of concentrated nitric acid and 3 ml of concentrated sulfuric acid. The mixture was stirred for 15 minutes in an ice bath and poured over 100 g of ice and water, filtered, washed, dried, dissolved in 40 ml of chloroform and chromatographed on alumina using successively 160 ml of hexane and 130 ml of chloroform. Evaporation gave 0.40 g (64%). Three recrystallizations (methanol) gave orange needles, mp 181-183°; ^{1}H nmr (deuteriochloroform): δ 9.72 (s, 1H at C-4), 9.00 (s, 1H at C-9), 8.56 (d, 1H at C-8, J = 7.0), 8.53 (d, 1H at C-6, J = 9.5), 7.73 (q, 1H at C-7); uv (1,4-dioxane): λ max, nm (ϵ), 249 (48,400), 347 sh (12,950), 352 (13,200), 362 (16,400), 436 (4,820), 460 sh (3,890).

Anal. Calcd. for $C_{10}H_5N_3O_2S$: C, 51.94; H, 2.16; N, 18.20. Found: C, 51.77; H, 2.15; N, 18.13.

Method B.

To an ice-cooled solution of naphtho[2,3-*c*][1,2,5]thiadiazole (0.25 g, 1.4 mmoles) in 5 ml of concentrated sulfuric acid was added a mixture of 0.1 ml of fuming nitric acid (d = 1.50) in 3 ml of concentrated nitric acid. After 5 minutes the reaction was worked up as above to give a 32% yield.

5-Aminonaphtho[2,3-*c*][1,2,5]thiadiazole.

Hydrogenation in a Parr apparatus at initial pressure of 40 psi of a mixture of 5-nitronaphtho[2,3-*c*][1,2,5]thiadiazole (0.40 g, 1.7 mmoles), 200 ml of absolute ethanol, 3 ml of glacial acetic acid, and 0.30 g of 5% Pd/C for 12 hours gave, after chromatography (see above), 0.23 g (66%) of product mp 150-170°. Four recrystallizations from methanol gave purple needles, mp 170-172°; ^{1}H nmr (acetone-d_6): δ 9.04 (s, 1H at C-4), 8.68 (s, 1H at C-9), 7.54 (q, 1H at C-6), 7.37 (t, 1H at C-7), 6.83 (q, 1H at C-8), 5.58 (broad, 2H, NH_2); uv (95% ethanol): λ max, nm (ε), 216 (30,800), 274 (29,200), 334 (5,030), 347 (5,630), 363 (5,770), 528 (1,950).

Anal. Calcd. for $C_{10}H_7N_3S$: C, 59.67; H, 3.48; N, 20.92; S, 15.93. Found: C, 59.93; H, 3.45; N, 20.86; S, 15.76 (by difference).

4-Chloro-8-nitronaphtho[2,3-*c*][1,2,5]thiadiazole.

Chlorine was bubbled into a solution of 5-nitronaphtho[2,3-*c*][1,2,5]thiadiazole (0.10 g, 0.43 mmoles) in 20 ml of acetic for 25 minutes. Evaporation of solvent gave a white solid (probably 4,9-dichloro-4,9-dihydro-5-nitronaphtho[2,3-*c*][1,2,5]thiadiazole) which upon recrystallization from acetone and then 95% ethanol gave 0.09 g (78%) of orange 4-chloro-8-nitronaphtho[2,3-*c*][1,2,5]-thiadiazole, mp 217-220°; ^{1}H nmr (deuteriochloroform): δ 9.50 (s, 1H at C-9), 8.90 (d, 1H at C-7, J = 9.5), 8.4 (d, 1H at C-5, J = 7.2), 7.74 (q, 1H at C-6); uv (95% ethanol): λ max, nm (ε), 210 (23,400), 254 (51,900), 330 (4,120), 348 (8,430), 362 (10,800), 459 (5,490), 470 (5,020).

Anal. Calcd. for $C_{10}H_4ClN_3O_2S$: C, 45.20; H, 1.51; N, 15.82. Found: C, 45.33; H, 1.46; N, 15.80.

REFERENCES AND NOTES

[1] M. Sainsbury in Rodd's Chemistry of Carbon Compounds, 2nd Ed, S. Coffey, ed, Vol **III^H**, 1979, p 18.

[2] M. Sainsbury in Rodd's Chemistry of Carbon Compounds, 2nd Ed, S. Coffey, ed, Vol **III^H**, 1979, p 17.

[3] V. G. Pesin, A. M. Khaletskii and L. A. Kaukhova, *J. Gen. Chem. U.S.S.R.*, **30**, 2167 (1960).

[4] M. P. Cava and R. H. Schlessinger, *Tetrahedron Letters*, 3815 (1964).