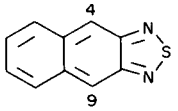
Halogenation of Naphtho[2,3-*c*]-1,2,5-thiadiazole

Walter T. Smith, Jr., Albert C. Kovelsky (1) and John M. Patterson

Department of Chemistry, University of Kentucky

Naphtho [2,3-*c*] 1,2,5 thiadiazole (I) may be regarded as a heterocyclic analog of anthracene and as a part of our study of the reactions of I we were interested in comparing the nature of the bromination and chlorination reactions with that of anthracene.



I

Treatment of compound I with bromine in carbon tetrachloride either at room temperature or refluxed one hour, with bromine in glacial acetic acid at room temperature, or with bromine in carbon disulfide at room temperature, gave an addition product identified as 4,9-dibromo-4,9-dihydronaphtho[2,3-*c*]-1,2,5-thiadiazole. The addition of phosphorus pentachloride, iron filings, and cuprous chloride to the bromination reactions had no effect on the yield or nature of the product.

The preferred catalyst for formation of 4,9-dibromonaphtho[2,3-*c*]-1,2,5-thiadiazole is zinc chloride. Thus, bromination of compound I in carbon tetrachloride in the presence of zinc chloride provides a convenient synthesis of 4,9-dibromonaphtho[2,3-*c*]-1,2,5-thiadiazole. When ferric chloride or stannic chloride was used as the catalyst in refluxing carbon tetrachloride, some impure 4,9-dibromonaphtho [2,3-*c*] 1,2,5 thiadiazole was formed.

Our results (summarized in Table I) indicate that the dibromodihydro product resulting from addition of bromine to compound I is much more stable than the corresponding bromine addition product of anthracene (2,3).

TABLE I

Reactions of Naphtho[2,3-*c*]-1,2,5-thiadiazole with Bromine (a)

Ratio of Br_2 to I	Catalyst	% of 4,9-dibromo-naphtho[2,3-*c*]-1,2,5-thiadiazole	% of 4,9-dibromo-4,9-dihydronaphtho [2,3-*c*]-1,2,5-thiadiazole
7:1 (b)	–	–	34
7:1	–	minor	major
1.4:1 (b,c)	–	–	62
5:1	2ml. $SnCl_4$	impure	–
5:1	0.1 g. PCl_5	trace	62
5:1	0.1 g. Fe filings (20 mesh)	trace	64
1.4:1	0.1 g. Fe filings (20 mesh)	none	64
1.4:1	0.1 g. $CuCl_2$	none	30
5:1	0.1 g. $ZnCl_2$	36-39	–
1.4:1	0.1 g. $ZnCl_2$	34	–
1.4:1	–	–	54
1.4:1	0.1 g. $FeCl_3$	impure	–
1.4:1 (b,d)	–	–	81

(a) Reaction conditions were 1 hour at 77° in carbon tetrachloride unless otherwise indicated. (b) Reaction temperature, 25°. (c) Acetic Acid, solvent. (d) Carbon disulfide, solvent.

The chlorination of naphtho[2,3-*c*]-1,2,5-thiadiazole with sulfuryl chloride gave 4,9-dichloronaphtho[2,3-*c*]-1,2,5-thiadiazole.

Treatment of naphtho[2,3-*c*]-1,2,5-thiadiazole with either chlorine in carbon tetrachloride at room temperature or chlorine in glacial acetic acid at 50° gave the unstable 4,9-dichloro-4,9-dihydronaphtho[2,3-*c*]-1,2,5-thiadiazole as the major product along with what is probably 4,9-dichloronaphtho[2,3-*c*]-1,2,5-thiadiazole as the minor product.

These results indicate that the chlorination of I is generally similar to the chlorination of anthracene (4).

EXPERIMENTAL

All melting points are uncorrected and were taken on a Fisher-Johns apparatus. The infrared spectra were obtained on a Beckman Model IR-8 Spectrophotometer and the ultraviolet spectra on a Perkin-Elmer Model 202 Spectrophotometer. The n.m.r. spectra were determined on a Varian HA-60-IL Spectrometer with a C-1024 time averaging computer, using tetramethylsilane as an internal standard. The elemental analyses were obtained on an F and M Model 185 Carbon Hydrogen Nitrogen Analyzer by Mr. Daryl Sharp at the University of Kentucky.

Preparation of 4,9-Dibromo-4,9-dihydronaphtho[2,3-*c*]-1,2,5-thiadiazole.

Method A.

To 0.25 g. (0.0014 mole) of naphtho[2,3-*c*]-1,2,5-thiadiazole, m.p. 97-99°, and 30 ml. dry carbon tetrachloride, a solution of 0.5 ml. (1.56 g., 0.009 mole) of bromine in 5 ml. carbon tetrachloride was added and the reaction mixture was stirred for one hour at room temperature. The reaction mixture was poured into a separatory funnel, washed with two 25-ml. portions of sodium thiosulfate solution, two 25-ml. portions of water, and dried over anhydrous sodium sulfate. After the drying agent was removed by filtration, the solvent was evaporated to one-fifth of its volume and chilled. Two recrystallizations from carbon tetrachloride gave 0.13 g. (34%) of 4,9-dibromo-4,9-dihydronaphtho[2,3-*c*]-1,2,5-thiadiazole, m.p. 160-162°; the n.m.r. spectrum (in a carbon tetrachloride-deuteriochloroform mixture) exhibited a multiplet centered at 7.57 ppm for 4H of the outer ring, and a singlet at 6.55 ppm for 2H due to the 4,9-aliphatic type protons; the ultraviolet spectrum (in 1,4-dioxane) showed λ max, mμ (ε), 255 (ε, 1300), 280 (ε, 16,100); the infrared spectrum (in chloroform) was consistent with the above compound.

Anal. Calcd. for $C_{10}H_6Br_2N_2S$: C, 34.70; H, 1.74; N, 8.10. Found: C, 34.50; H, 1.98; H, 8.25.

Method B.

A mixture of 0.20 g. (0.001 mole) of naphtho[2,3-*c*]-1,2,5-thiadiazole, m.p. 97-99°, 0.10 g. of the appropriate catalyst, and 30 ml. dry carbon tetrachloride was heated to reflux temperature and then a solution of bromine (see Table I) in 5 ml. of carbon tetrachloride was added through the top of the condenser. The mixture was refluxed for one hour, cooled, and the excess bromine was allowed to evaporate in the hood. The solution was heated, treated with Norit, and the volume of the solvent was reduced. Upon cooling there was obtained 4,9-dibromo-4,9-dihydronaphtho[2,3-*c*]-1,2,5-thiadiazole. Additional recrystallizations from carbon tetrachloride gave material which showed no depression of melting point with the compound obtained by Method A.

Preparation of 4,9-Dibromonaphtho[2,3-*c*]-1,2,5-thiadiazole.

A 5:1 ratio of bromine to naphtho[2,3-*c*]-1,2,5-thiadiazole was used. The procedure was the same as described in Method B. There was obtained 36-39% of 4,9-dibromonaphtho[2,3-*c*]-1,2,5-thiadiazole, m.p. 238-240° as bright red needles from carbon tetrachloride. The ultraviolet spectrum (in 1,4-dioxane) showed λ max mμ (ε), 261(ε, 55,600), 335(ε, 3,830), 352(ε, 6,900), 367(ε, 9,960), 470(ε, 5,700), 490(ε, 5,360). The n.m.r. spectrum (in deuteriochloroform) exhibited an AA′BB′ pattern as shown in Emsley, Feeney, and Sutcliffe (5). The AA′ portion showed a complex multiplet centered at 8.46 ppm whereas the BB′ portion showed a complex multiplet centered at 7.62 ppm. A 50 cps expansion of the AA′ portion on a degassed sample showed 12 lines with the outer lines being weak.

Anal. Calcd. for $C_{10}H_4Br_2N_2S$: C, 34.90; H, 1.16; N, 8.13. Found: C, 34.77; H, 1.08; N, 8.15.

Preparation of 4,9-Dichloronaphtho[2,3-*c*]-1,2,5-thiadiazole.

A mixture of 0.25 g. (0.0014 mole) of naphtho[2,3-*c*]-1,2,5-thiadiazole, m.p. 97-99°, and 10 ml. (16.70 g., 0.12 mole) of sulfuryl chloride was heated at reflux temperature for 0.5 hour on a steam cone and then the excess sulfuryl chloride was boiled off. The solid was taken up in a methanol-acetone mixture, treated with Norit, and the acetone was evaporated to give 0.14 g. (41%) of 4,9-dichloronaphtho[2,3-*c*]-1,2,5-thiadiazole, m.p. 210-217°. Two additional recrystallizations from methanol gave a product melting at 215-217°. The n.m.r. spectrum (in deuteriochloroform) exhibited an AA′BB′ pattern (5). The AA′ portion showed a complex multiplet centered at 8.44 ppm whereas the BB′ portion showed a complex multiplet centered at 7.63 ppm. The ultraviolet spectrum (in 1,4-dioxane) showed λ max, mμ (ε), 262 (ε, 68,120), 335(ε, 3,760), 352(ε, 6,790), 367(ε, 9,270), 471(ε, 5,150), 490(ε, 4,790).

Anal. Calcd. for $C_{10}H_4Cl_2N_2S$: C, 47.10; H, 1.57; N, 10.96. Found: C, 46.73; H, 1.53; N, 10.91.

Preparation of 4,9-Dichloro-4,9-dihydronaphtho[2,3-*c*]-1,2,5-thiadiazole.

Method A.

Chlorine gas was bubbled into a solution of 0.25 g. (0.0014 mole) of naphtho[2,3-*c*]-1,2,5-thiadiazole, m.p. 97-99°, and 20 ml. dry carbon tetrachloride for 15 minutes at room temperature and then the mixture was stirred for an additional 45 minutes at room temperature. The solution was poured into a beaker and the solvent was evaporated in the hood. The solid was recrystallized from Skelly-solve B twice to remove a minor orange contaminant. The major product was a white solid which melted at 170-190° after two additional recrystallizations from methanol. There was obtained 0.14 g. (40%) of 4,9-dichloro-4,9-dihydronaphtho[2,3-*c*]-1,2,5-thiadiazole. It decomposed on standing in air. The minor product was believed to be 4,9-dichloronaphtho[2,3-*c*]-1,2,5-thiadiazole.

The n.m.r. spectrum of the white solid (in deuteriochloroform) exhibited a multiplet centered at 7.53 ppm for 4H of the outer ring, and a singlet at 6.30 ppm for 2H due to the 4,9-aliphatic-type protons. The ultraviolet spectrum (in 1,4-dioxane) showed λ max, mμ (ε), 247(ε, 6,450), 270(ε, 14,900), 273(ε, 15,000).

Anal. Calcd. for $C_{10}H_6Cl_2N_2S$: C, 46.65; H, 2.34; N, 10.90. Found: C, 46.90; H, 2.37; N, 10.93.

Method B.

A solution of 0.25 g. (0.0014 mole) of naphtho[2,3-*c*]-1,2,5-thiadiazole, m.p. 97-99°, and 25 ml. of glacial acetic acid was heated to 50° and then chlorine gas was bubbled in for 15 minutes. The reaction mixture was cooled and the acetic acid was evaporated in the hood. The solid was taken up in acetone, treated with Norit, and the acetone was replaced by methanol before cooling. There was obtained 0.17 g. (47%) of a white solid, probably 4,9-dichloro-4,9-dihydronaphtho[2,3-*c*]-1,2,5-thiadiazole, m.p. 120-170°. A trace amount of an orange solid present was believed to be 4,9-dichloronaphtho[2,3-*c*]-1,2,5-thiadiazole, m.p. 195-213°

Acknowledgment.

The authors wish to express their appreciation to Dr. Stanford L. Smith for assisting in the interpretation of the n.m.r. spectra.

REFERENCES

(1) From the Ph. D. dissertation of A. C. Kovelesky, University of Kentucky, 1967.

(2) P. Bercot, *Ann. Chim. (Paris)*, 6, 193 (1961); *Chem. Abstr.*, 56, 10058 (1962).

(3) E. DeB. Barnett, and J. W. Cook, *J. Chem. Soc.*, 125, 1084 (1924).

(4) M. A. Iljinsky, and B. I. Afremoff, *Ber.*, 69, 1824 (1936).

(5) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Spectroscopy," Vol. I, 404, Pergamon Press, Inc., New York, N. Y., 1965.

Received November 9, 1967 Lexington, Kentucky 40506