INVESTIGATION OF 2,1,3-THIA- AND 2,1,3-SELENADIAZOLE S
LXVII.* NITRATION OF NAPHTHO[1,2-d][2,1,3]THIADIAZOLE

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The nitration of naphtho[1,2-d][2,1,3]thiadiazole under the conditions that are normally used for aromatic compounds gives a mixture of 6- and 9-nitronaphthothiadiazoles, which can be reduced to 6- and 9-amino derivatives, respectively. 6-Hydroxynaphthothiadiazole is obtained from 6-aminophothothiadiazole by the Sandmeyer reaction, while 8-hydroxynaphthothiadiazole is converted to the 8-amino derivative under the conditions of the Bucherer reaction. 4-Carboxy-5-(o-carboxyphenyl)-2,1,3-thiadiazole was obtained by the oxidation of naphtho[1,2-d][2,1,3]-thiadiazole with a potassium dichromate-dilute sulfuric acid mixture.

In developing our research on the reactivity of condensed 2,1,3-thiadiazole systems, we turned to a study of the substitution reactions of naphtho[1,2-d][2,1,3]-thiadiazole (I) [2].

In the present paper we report the results of a study of the nitration of I.

A mixture of two isomeric nitro derivatives - 6-nitro- (II) and 9-nitronaphthothiadiazole (III) - is formed in high yield when I is nitrated with a nitrating mixture. Isomer II is the chief reaction product, and a small amount of III can be isolated only by chromatography.

The 6-amino (IV) and 9-aminonaphthothiadiazoles (V) obtained from nitro derivatives II and III can be separated by fractional crystallization; we used this method to establish the structure of nitro compounds II and III. Amines IV and V were converted to the corresponding chlorides and bromides† by means of the Sandmeyer reaction, while amine IV was converted to the corresponding hydroxy derivative (VI).

The position of the nitro group in II was determined by means of its oxidation products and by data from a study of amine IV.

*See [1] for communication LXVI.
†See the following communication for information regarding the chloro- and bromonaphthothiadiazoles.
m-Nitrobenzoic acid was isolated from the oxidation of nitro compound II with potassium permanganate in the presence of alkali; this result corresponds to four possible positions for the nitro group (isomeric structures II, III, VII, and VIII). 3-Nitrophthalic acid was isolated when the reaction was carried out without alkali; the formation of this acid shows that the nitro group occupies either the 6 or 9 positions. To solve this problem, we synthesized amine IV by the reaction of thionylaniline with 1,2,5-triaminonaphthalene (IX) [3]. In view of the fact that triamine IX is formed in very low yield, the aminonaphthothiadiazole (IV) obtained from it was not isolated in pure form. Spots with identical Rf values were detected when the latter was chromatographed in the presence of amine IV, obtained from nitro compound II.

Additional proof was obtained in a comparison of amine IV (the product of the reduction of nitro derivative II) with the three other isomeric 7- (X), 8- (XI), and 9-aminonaphthothiadiazoles (V), obtained by alternative synthesis by the reaction of thionylaniline with 1,2,6- [4], 1,2,7- [5], and 1,2,8-triaminonaphthalenes [6], respectively. Amine IV had properties (melting point and UV and IR spectra) that differed from those of amines X, XI, and V. Amine XI was also obtained by the Bucherer reaction [7] by heating the 8-hydroxy derivative of I (XII) with a mixture of ammonium bisulfite and 25% ammonium hydroxide. Hydroxynaphthothiadiazole XII was obtained by the reaction of thionylaniline with 1,2-diamino-7-hydroxynaphthalene [8].

The position of the nitro group in III was proved by comparison of the amine (V) obtained from it with the analogous amine obtained from 1,2,8-triaminonaphthalene and also by comparison of the spectra of amine V (obtained from III) and of the same amine obtained by the reaction of 1,8-naphthalenediamine with sulfur nitride [9].

The preparation of amine V by the reaction of 1,2,8-triaminonaphthalene with thionylaniline is worthy of attention. In this reaction, one might have expected the formation of 2-aminonaphtho[1,8-c,d][1,2,6]-thiadiazine [10-12].

The predominant occurrence of the reaction via direction 1 shows that the formation of the thiadiazole ring is preferred over the formation of the thiadiazine ring.

The results of the nitration of I can be explained when the latter is considered as an α,β-disubstituted naphthalene. As a structural element of the benzo-2,1,3-thiadiazole system, the thiadiazole ring has an electron-withdrawing effect in electrophilic and nucleophilic substitution reactions [13-15]. It is therefore natural when likening I to a disubstituted naphthalene to turn for comparison to α,β-disubstituted naphthalenes that contain electron-withdrawing substituents. It is known [16] that in the electrophilic substitution reactions of β-halo and (partially) α-halo-, α- and β-sulfo-, and α- and β-nitronaphthalenes, the next substituent enters primarily the ring that is not bonded to the substituent; in this case the substituent enters primarily the 5 and 8 positions and, less frequently, the 5 and 7 positions. This is explained by deactivation of the ring attached to the electron-acceptor substituent.

Thus the nitration of I, which leads to a mixture of isomeric 6- and 9-nitro derivatives, proceeds in the same way as the nitration of naphthalene derivatives with electron-acceptor substituents. Naphth[1,2-d]-[2,1,3]oxadiazole [17] is similarly nitrated.

Above it was pointed out that 3-nitrophthalic and m-nitrobenzoic acids are formed by the action of potassium permanganate on nitro compound II; i.e., the benzene ring bonded to the thiadiazole ring and the heteroring itself primarily undergo attack. When benzothiadiazole is oxidized under these conditions, the benzene ring attached to the thiadiazole ring is oxidatively cleaved to give 4,5-dicarboxy-2,1,3-thiadiazole [13-15]. The lower resistance to oxidizing agents of polycyclic heteroaromatic systems as compared with the stability of one- and two-ring systems is an expression of their weakened aromaticity.

No appreciable changes are observed when a potassium dichromate-dilute sulfuric acid mixture or chromic anhydride in concentrated sulfuric acid act on II. Under similar conditions (with the dichromate