Registry No.—**3**, 16205-74-6; **4**, 7007-34-3; **5**, 16205-76-8; **6**, 16205-77-9; **7**, 16205-78-0.

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Synthesis and Proof of Structure of 2,6-Diaminobenzo[1,2-*d*:4,5-*d*′]bisthiazole

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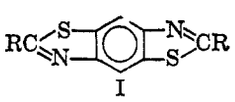
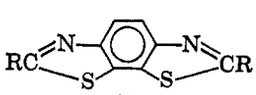
The first reported synthesis of benzo[1,2-*d*:4,5-*d*′]-bisthiazoles (I) was that of Green and Perkin[1] in 1903. Since that time, several other workers[2-12] have discussed the synthesis or reactions of these compounds. In each of these cases, either no proof of structure was given, or reference was made to Green and Perkin, who base their structure on the presumed 1,2,4,5 configuration of the intermediate diaminobenzenedithiosulfonic acid. However, the latter workers made no attempt to prove the structure of this compound. Nowhere in



I



II

the literature is the synthesis of any benzo[1,2-d:4,3-*d*′]bisthiazoles (II) claimed. However, we have recently found that the previously reported benzobisthiazoles are actually II rather than I. We have also found that 2,6-diaminobenzo[1,2-*d*:4,5-*d*′]bisthiazole (Ia, R = NH_2) may be prepared by a modified Hugershoff[13] reaction.

Compound Ia is prepared by the ring closure of *p*-phenylenebisthiourea using bromine in chloroform according to the procedure of Barnikow, *et al.*,[14] for the *meta* isomer. This is the first confirmed synthesis of a "linear" benzobisthiazole from *p*-phenylenediamine.

2,7-Diaminobenzo[1,2-*d*:4,3-*d*′]bisthiazole (IIa, R = NH_2), the "angular" compound, was prepared from 1,4-diaminobenzene-2,3-dithiosulfonic acid by the method

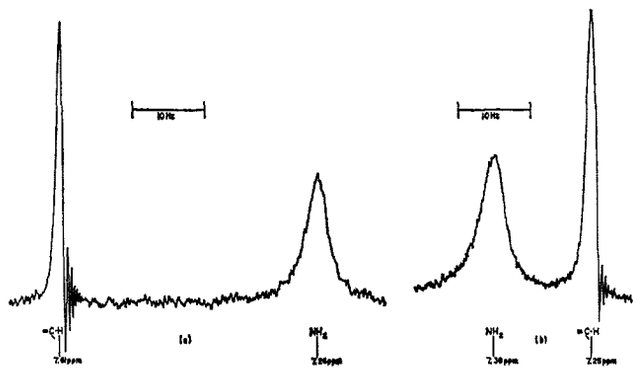


Figure 1.—(a) Normal 100-MHz nmr spectrum of compound Ia; (b) normal 100-MHz nmr spectrum of compound IIa. Sweep rate is 1 Hz/sec.

of Stephens and Wibberly[6] and also by the reaction of *p*-phenylenediamine, ammonium thiocyanate, and bromine in acetic acid according to the procedure of Sureau and Alicot.[10] The products (mp > 350°) from both methods are identical. This unequivocally establishes the structure of the diaminobenzenedithiosulfonic acid prepared by Green and Perkin[1] as 1,4-diaminobenzene-2,3-dithiosulfonic acid instead of the reported 1,4-diaminobenzene-2,5-dithiosulfonic acid.

The structural assignments were made on the basis of nmr spectra. Because of the symmetry of the proposed molecular structures, both compounds Ia and IIa have a normal spectrum consisting of two absorptions only (Figure 1): a narrow line representing the aromatic protons and a relatively broad line corresponding to the amine hydrogens; the integrated intensities are in the ratio 1:2, respectively. In compound Ia, the aromatic absorption appears downfield of the amine band at 7.61 ppm (δ scale); while in IIa, the aromatic protons are shifted to 7.25 ppm and occur on the high-field side of the NH_2 peak. Because of the various factors contributing to electronic shielding in these closely related molecules, any assignment of structure on the sole basis of chemical shifts would be tenuous at best.

The symmetrical structures may be distinguished unambiguously, however, from the C^{13} satellite spectra. When one aromatic hydrogen is bonded to a C^{13} atom, the magnetic equivalence of the two protons in the ring is destroyed. (Under conditions of natural abundance, the probability that both protons are attached to C^{13} is negligible.) The resulting satellite spectrum[15,16] corresponds to the AB portion of an ABX spin system, which now manifests the proton–proton coupling constant, J_{AB}. The latter enables us to discern whether the protons are *ortho* or *para* to one another.

The four innermost lines of the satellite spectrum lie close to the predominant C^{12}–H resonance, and are obscured by it. Since $J_{C^{13}-H} \approx 160$ Hz for an aromatic system, however, we may still investigate the pairs of lines which appear about 80 Hz on either side of the normal aromatic signal.

The limited solubility of the compounds and the low natural abundance of carbon-13 (1.1%) necessitate the use of signal enhancement techniques. Figure 2 depicts the time-averaged spectra—after 400 successive

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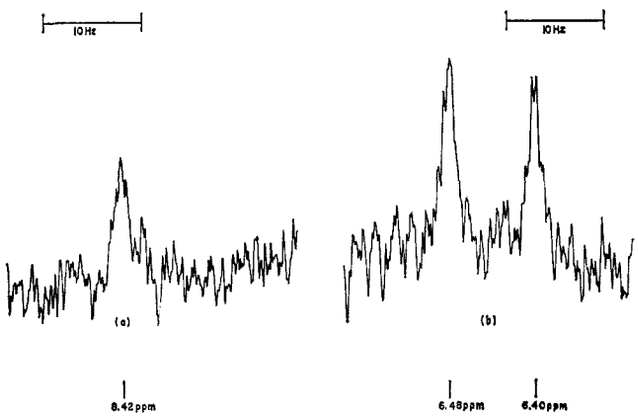

Figure 2.—Time-averaged nmr spectra, after 400 scans. Sweep rate is 1 Hz/sec: (a) compound Ia, region 80 Hz downfield of normal aromatic signal; (b) compound IIa, region 80 Hz upfield of normal aromatic signal. (Regions were chosen so as to avoid interference with the enhanced spinning side bands of the NH_2 peak.)

scans or 20-fold improvement in sensitivity—of the aforementioned satellite regions in compounds Ia and IIa. In Figure 2b, two lines with 8 Hz spacing (J_{AB}) are clearly observed, and IIa may be readily assigned to the structure bearing protons in an *ortho* relationship. In compound Ia (Figure 2a), the interaction between the *p*-hydrogens is a fraction of a Hz, and the satellite pattern consists essentially of a single, unresolved absorption.

Experimental Section[17]

2,6-Diaminobenzo[1,2-*d*:4,5-*d'*]bisthiazole.—A solution of 147 g (0.92 mol) of bromine in 200 ml of dry chloroform was slowly added, with stirring, to a suspension of 100 g (0.44 mol) of *p*-phenylenebisthiourea[18] in 1000 ml of dry chloroform in a round-bottom flask. The addition required 1 hr and the mixture was stirred at room temperature for an additional 4 hr. It was then refluxed 16 hr. After cooling, the solids were filtered off, washed with chloroform, and air dried. The product was converted into the free base by suspending it in 1 l. of 2 *N* ammonium hydroxide solution for 10 min, filtering, and washing with distilled water until the washings were neutral. Purification was accomplished by digestion in hot dimethylformamide for 30 min, cooling, filtering, and washing with acetone. The product, which was obtained in 35.8% yield, had a mp > 350°; ultraviolet maxima (80% acetic acid), 313 mμ (ε 13,900), 283 mμ (ε 15,600), 238 mμ (ε 35,600).

Anal. Calcd for $C_8H_6N_4S_2$: C, 43.23; H, 2.72; N, 25.21; S, 28.85. Found: C, 43.02; H, 2.61; N, 25.26; S, 28.79.

2,7-Diaminobenzo[1,2-*d*:4,3-*d'*]bisthiazole (a) from 1,4-diaminobenzene-2,3-dithiosulfonic acid[6] showed ultraviolet maxima (80% acetic acid) at 291 mμ (ε 18,600) and 245 mμ (ε 35,800) (*Anal.* Found: C, 43.17; H, 2.89; N, 25.10; S, 29.04) and (b) from *p*-phenylenediamine, ammonium thiocyanate, and bromine[10] was identical with (a) shown by ir and uv spectra.

The nmr spectra were obtained on a Varian HA-100 spectrometer, utilizing the Varian Autoshim accessory and the C-1024 time-averaging computer. The compounds were examined as saturated solutions in dimethyl sulfoxide-d_6, while dissolved TMS was used as the internal locking signal and chemical shift reference. The 400 time-averaged scans required approximately 13 hr.

Registry No.—Ia, 16162-28-0; IIa, 16203-56-8.

Acknowledgments.—We are indebted to Drs. W. A. Hewett and J. N. Shoolery for their helpful discussions during the course of this investigation.

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Facile Synthesis of 1,3-Oxathiolanes from Ketones and 2-Mercaptoethanol[1]

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We wish to report a convenient and efficient synthesis of 1,3-oxathiolanes. We have found that the condensation of equimolar mixtures of carbonyl compound and 2-mercaptoethanol in dilute ether solution is readily effected by 1 equiv of boron trifluoride. The boron trifluoride scavenges the water formed and is converted into its mono- or dihydrate. The use of several other catalysts has been reported.[3,4] The oxathiolanes of three sterodial ketones have been synthesized by Fieser[5] in a condensation using excess quantities of boron trifluoride and 2-mercaptoethanol per mole of ketone in acetic acid.

In almost all cases we have examined (Table I) the yields obtained using the boron trifluoride–ether system have been better than those obtained by the generally used *p*-toluenesulfonic acid–benzene azeotrope method.[4] In particular, by the boron trifluoride method a 56% yield of pure, crystalline 2,2-diphenyl-1,3-oxathiolane can be gained easily in 3 hr. By contrast, using the azeotrope method,[4] Marshall and Stevenson[6] observed much polymer formation and experienced difficulties in obtaining even a 28.5% yield. We have been unable to effect the condensation using di-*t*-butyl ketone; however, diisopropyl ketone proceeds to oxathiolane normally. The condensation with norbornanone led to a mixture of isomers.

Reducing the amount of solvent for the condensations much below 750 ml per mole of ketone leads to greatly reduced yields of oxathiolanes and an increase in quantities of ether-insoluble, apparently polymeric materials. Similarly the presence of even a residual trace of boron trifluoride in the crude product after washing causes the oxathiolanes to decompose rapidly to the ketone and a gummy, apparently polymeric residue when distillation is attempted. The oxathiolanes themselves are generally stable toward distillation or heating under reflux for at least 2 days.[7]

When the amount of boron trifluoride used for the formation of the oxathiolane from cycloheptanone was reduced to a 2:3 molar ratio, the per cent conversion was reduced from 92 to 74% and attained only 82% when the reaction time was eight times longer. The per cent yield based on unrecovered cycloheptanone

(1) Acknowledgement is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support (Grant No. 209-G) of this research.

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