

ml of carbon tetrachloride was added NBS (1.43 g, 0.008 mole). The mixture was refluxed for 10 hr and cooled. Precipitate **4** was removed by filtration and recrystallized from ethanol to afford 1.22 g (46%), mp 210–212°. Further recrystallization from benzene gave material of mp 212–213°; infrared indicated $\nu_{\text{max}}^{\text{KBr}}$ 1730 (C=O), 1300 (CH₂), and 1130 (C—O) cm⁻¹; nmr (CDCl₃) showed 2.97 (singlet) and 6.7–8.1 ppm (multiplet) in the ratio 1:1.5.

Anal. Calcd for C₁₄H₁₀BrNO₂S: C, 50.00; H, 2.98. Found: C, 50.02; H, 2.87.

Titration of 4.—According to the method of Groebel⁴ an iodometric titration was performed on **4**. The titrated equivalent weight was 342 (calcd 336). Bis(1-bromo-2-naphthyl) disulfide (**5**) was isolated after the titration, mp 160–161° (lit.¹³ mp 160–161°).

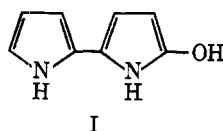
On the Hydrogen Peroxide Oxidation Product of Pyrrole. Synthesis of 5-(2-Pyrrolyl)-2-pyrrolidone

HARRY H. WASSERMAN AND MARCEL EBERLE

Department of Chemistry, Yale University,
New Haven, Connecticut

Received September 30, 1966

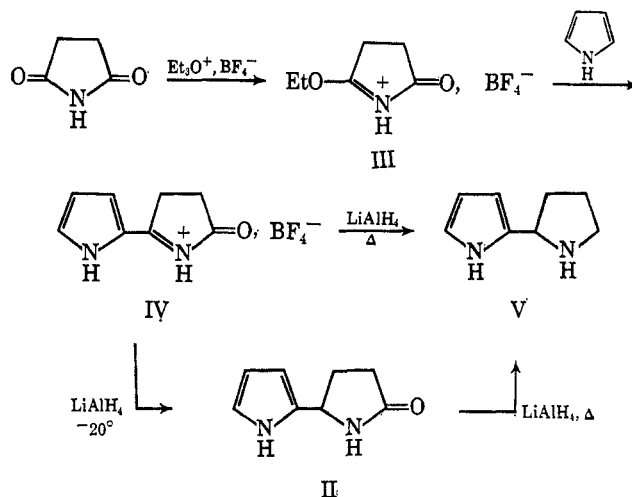
The oxidation of pyrrole by hydrogen peroxide in acetic acid produces a crystalline substance, C₈H₁₀N₂O, mp 136°, which was first observed by Angeli¹ and later investigated by Pieroni.² This compound, one of the simplest oxidation products of pyrrole, has been of special interest as a possible intermediate in the formation of pyrrole blacks.² Pieroni's studies culminated in the assignment of I, 5-hydroxy-2,2'-bipyrrole, or a tautomer, to this so-called "oxybipyrrole."



Structure I was generally accepted until the very recent studies of Chierici and Gardini³ who reinvestigated the oxidation product with the aid of infrared, ultraviolet, and nmr techniques. Based on their new spectroscopic evidence these authors concluded that II must, instead, be correct.

During studies on bipyroles related to prodigiosin⁴ we have prepared 5-(2-pyrrolyl)-2-pyrrolidone (II) by an independent method outlined below. Our synthetic pyrrolidone is identical in every respect with the Angeli hydrogen peroxide-pyrrole oxidation product. This evidence thus confirms the structural assignment of Chierici and Gardini.

Treatment of succinimide with triethyloxonium fluoroborate⁵ in methylene chloride for 12 hr at room temperature yielded the imino ester salt (III) which readily reacted with pyrrole to form an acidic, crystalline addition product (IV). The infrared spectrum of salt IV shows two strong bands in the double-bond



region at 1780 (carbonyl) and 1600 cm⁻¹ (protonated imino group). The molecular weight is in accord with the composition, C₈H₈ON₂·HBF₄.

Reaction of IV with lithium aluminum hydride at -20° resulted in partial reduction to the lactam II. The latter was found to be indistinguishable⁶ (infrared, nmr, mixture melting point) from the hydrogen peroxide oxidation product of pyrrole, prepared according to the procedure reported by Chierici and Gardini.³

Reduction of salt IV at elevated temperatures, or further reduction of pyrrolylpyrrolidone II by lithium aluminum hydride yielded 2,2'-pyrrolylpyrrolidine (V), identical in all respects with the known product.^{7,8}

Experimental Section⁹

5-(2-Pyrrolyl)-2-pyrrolidone.—Triethyloxonium fluoroborate (10.6 g) was prepared by the method of Meerwein⁹ from 11.5 g of boron trifluoride etherate and 5.5 g of epichlorohydrin. The oxonium salt was dissolved in 30 ml of methylene chloride and 5.5 g (0.054 mole) of succinimide was added. Stirring of the reaction mixture was continued overnight and the solution was cooled with ice and then treated with 3.8 g of pyrrole (0.057 mole). The material which precipitated was removed by filtration after 10 min yielding 10.3 g (78%) of crystalline fluoroborate salt. A sample recrystallized three times from acetone-hexane melted at 192°, pK = 6.5. The infrared spectrum (KBr) showed peaks at 3275, 3125, 1780, 1600, and 1505 cm⁻¹. The ultraviolet absorption spectrum had $\lambda_{\text{max}}^{\text{EtOH}}$ 335 m μ . *Anal.* Calcd: mol wt, 236. Found (titrimetric): mol wt, 232.

To a suspension of lithium aluminum hydride (1 g) in 25 ml of anhydrous ether, cooled in an ice-salt mixture, was gradually added 1 g of the above fluoroborate salt. The reaction mixture was stored for 2 hr at -20°. The excess hydride reagent was destroyed by addition of water in small portions, more ether (25 ml) was added, and after filtration, the solvent was gradually removed under vacuum. From the solution, 395 mg (62%) of lactam was obtained. After recrystallization three times from acetone-petroleum ether (bp 60–80°) the product melted at 138°. *Anal.* Calcd for C₈H₁₀N₂O: C, 63.98; H, 6.71; N, 18.65. Found: C, 64.04; H, 6.83; N, 18.52. The infrared spectrum (CHCl₃) showed peaks at 3475, 3430, 1690, and 1560 cm⁻¹. This material was shown to be identical (nmr, infrared, mixture melting point) with the product obtained by the oxidation of

(6) We wish to thank Mr. Gordon Guthrie for repeating the hydrogen peroxide preparation of II³ and for making the comparison of the two products.

(7) D. W. Fuhlhage and C. A. VanderWerf, *J. Am. Chem. Soc.*, **80**, 6249 (1958).

(8) J. H. Atkinson, R. Griggs, and A. W. Johnson, *J. Chem. Soc.*, 893 (1964).

(9) Melting points are uncorrected. Nmr spectra were determined with a Varian A-60 spectrometer. Infrared analyses were run on a Perkin-Elmer Model 421 spectrometer.

(1) A. Angeli and C. Lutri, *Gazz. Chim. Ital.*, **50**, 128 (1920).

(2) A. Pieroni and A. Moggio, *ibid.*, **53**, 126 (1923), and earlier papers.

(3) L. Chierici and G. P. Gardini, *Tetrahedron*, **22**, 53 (1966).

(4) H. H. Wasserman, J. E. McKeon, L. Smith, and P. Forgiione, *J. Am. Chem. Soc.*, **82**, 506 (1960).

(5) H. Meerwein, W. Florian, N. Schön, and G. Stopp, *Ann.*, **641**, 1 (1961).

pyrrole with hydrogen peroxide in acetic acid according to the method of Chierici and Gardini.³

2,2'-Pyrrolylpyrrolidine.—The 5-(2-pyrrolyl)-2-pyrrolidone (150 mg) prepared as described above was added to a solution of 500 mg of lithium aluminum hydride in ether (25 ml). The mixture was stirred at room temperature for 1 hr and then refluxed for 15 min. Excess reducing agent was destroyed by the slow addition of water, an additional 25 ml of ether was added, and the solution was filtered. Evaporation of solvent yielded 82 mg (60%) of product, mp 86° after vacuum sublimation (lit.⁸ mp 85.5–86.5°). The 2,2'-pyrrolylpyrrolidine was identical (mixture melting point and infrared) with the product prepared independently by the reduction of 2,2'-pyrrolylpyrrolone using the method of Atkinson and co-workers.³ The same product could also be obtained from fluoroborate salt IV by stirring for 1 hr with lithium aluminum hydride at room temperature followed by refluxing for 15 min.

Acknowledgment.—This work was supported in part by Grant AI-04798 from the National Institutes of Health.

Optical Rotatory Dispersion of Some Cyclic Sulfides¹

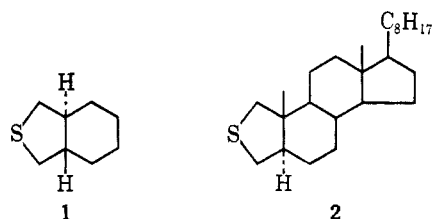
P. LAUR², H. HÄUSER, J. E. GURST, AND KURT MISLOW

Department of Chemistry, Princeton University,
Princeton, New Jersey 08540

Received October 6, 1966

The optical rotatory dispersion (ORD) and circular dichroism properties of simple organic sulfides have not been studied in detail. Cotton effects have been measured in episulfides,^{3–5} 1,3-oxathiolanes,^{5,6} 1,3-dithiolanes,⁶ and 1,3-oxathianes,⁶ but in these compounds special electronic effects may be operative.^{4–7} ORD investigations of carbohydrate sulfides⁸ and of thio ether derivatives of cysteine and 4-thialysine⁹ have been restricted to the range of wavelengths above 265 and *ca.* 300 m μ , respectively, furnishing plain dispersion curves only. In the circular dichroism of a series of D-(+)-alkylthiosuccinic acids, a first dichroic absorption band was reached with λ_{\max} *ca.* 240 m μ (ORD peak at *ca.* 250 m μ),¹⁰ but interpretation and analysis of the data are made difficult by the presence of the carboxyl chromophore which has similar transition energy.

To study the optical properties of dialkyl sulfides, we synthesized the conformationally rigid compounds 1 and 2 with known and *opposite* absolute configuration at the 5–6 ring juncture. Compound 1, (–)-



(*8R,9R*)-*trans*-2-thiahydrindan, was prepared from (+)-*trans*-cyclohexane-1,2-dicarboxylic acid (obtained by resolution¹¹ of the racemic acid) *via* reduction of the diacid to the diol, tosylation, and ring closure with sodium sulfide. Since the absolute configuration of (+)-*trans*-cyclohexane-1,2-dicarboxylic acid is known to be (*S,S*) by correlation with (–)-(*8R,9R*)-*trans*-hexahydroindan-2-one,¹¹ the absolute configuration of 1 is established unambiguously. Since A-nor-2-thiacholestane (2), was prepared from cholesterol *via* cholestan-3 β -ol and the 2,3-secocholestane-2,3-dioic acid, the absolute configuration of 2 is that shown in the formula above.

In Figure 1 are presented the ultraviolet absorption characteristics of sulfides 1 and 2. In acetonitrile solution each compound displays two absorption bands: *ca.* 205 m μ (ϵ 1790) and 215 m μ (ϵ 1480) [shoulder (sh)] in 1, and *ca.* 205 m μ (ϵ 1810) (sh) and 215 m μ (ϵ 1370) (sh) in 2. In addition, low-intensity absorption was observed between λ *ca.* 230 and 260 m μ . This consistently observed feature in the ultraviolet absorption curve indicates the presence of an electronic transition at *ca.* 240–245 m μ (ϵ *ca.* 50). The presence of a low-intensity absorption band near 240 m μ in tetramethylene sulfide (tetrahydrothiophene) and other simple sulfides has been previously noted^{7,12} and discussed.¹²

In a further refinement of our data, the ultraviolet spectra were decomposed by a nonlinear least-squares curve-fitting computer program¹³ into component bands; the long wavelength transition thus dissected out of the tails of the shorter wavelength bands has $\lambda_{\max}^{\text{acetonitrile}}$ 244.3 m μ (ϵ 53.6) (half band width 10.4 m μ) and $\lambda_{\max}^{\text{acetonitrile}}$ 245.1 m μ (ϵ 67.8) (half band width 11.1 m μ) for 1 and 2, respectively. This transition proved to be strongly optically active and characteristic of configuration as detailed below.

Inspection of the ORD curve of 1 (Figure 2) reveals a strong negative Cotton effect with a midpoint at about 240 m μ (the second extremum is seen as a shoulder at *ca.* 230 m μ), followed by a positive effect (midpoint at about 218 m μ) and a negative one (midpoint at about 205 m μ). Decomposition of the ORD curve through use of the computer program recently described by Carver, Shechter, and Blout¹⁴ yielded two Cotton effects, one centered at 243 m μ ($R = -3.86 \times 10^{-40}$ erg cm³) and one at 217 m μ ($R = +3.48 \times 10^{-40}$ erg cm³).

Inspection of the ORD curve of 2 (Figure 2) reveals two positive Cotton effects of comparable amplitudes,

(1) This work was supported by the National Science Foundation under Grant No. GP-3375.

(2) Department of Organic Chemistry, Weizmann Institute of Science, Rehovoth, Israel.

(3) C. Djerassi, H. Wolf, D. A. Lightner, E. Bunnenberg, K. Takeda, T. Komeno, and K. Kuriyama, *Tetrahedron*, **19**, 1547 (1963).

(4) D. E. Bays, R. C. Cookson, R. R. Hill, J. F. McGhie, and G. E. Usher, *J. Chem. Soc.*, 1563 (1964).

(5) K. Kuriyama, T. Komeno, and K. Takeda, *Tetrahedron*, **22**, 1039 (1966).

(6) D. A. Lightner, C. Djerassi, K. Takeda, K. Kiriyaama, and T. Komeno, *ibid.*, **21**, 1581 (1965).

(7) E. A. Fehnel and M. Carmack, *J. Am. Chem. Soc.*, **71**, 84 (1949); *cf.* H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p 475.

(8) Y. Tsuzuki, K. Tanabe, M. Akagi, and S. Tejima, *Bull. Chem. Soc. Japan*, **38**, 270 (1965).

(9) K. Blaha, I. Frič, and P. Hermann, *Collection Czech. Chem. Commun.*, **30**, 304 (1965).

(10) A. Fredga, J. P. Jennings, W. Klyne, P. M. Scopes, B. Sjöberg, and S. Sjöberg, *J. Chem. Soc.*, 3928 (1965).

(11) D. E. Applequist and N. D. Werner, *J. Org. Chem.*, **28**, 48 (1963).

(12) L. B. Clark and W. T. Simpson, *J. Chem. Phys.*, **43**, 3866 (1965); S. D. Thompson, D. G. Carroll, F. Watson, M. O'Donnell, and S. P. McGlynn, *ibid.*, **45**, 1367 (1966).

(13) H. Stone, *J. Opt. Soc. Am.*, **52**, 998 (1962). We are indebted to Mr. M. Goldstein and Dr. J. Jacobus for performing the computations.

(14) J. P. Carver, E. Shechter, and E. R. Blout, *J. Am. Chem. Soc.*, **88**, 2550 (1966). We are indebted to Professor Blout for kindly providing us with details of this program prior to publication, and to Mr. M. Goldstein and Dr. J. Jacobus for performing the computations.