the aqueous solution was refluxed for 3.5 hr. before cooling. Filtration gave 0.52 g., m.p. 99–102°; mixed m.p. with the starting material, 101–102.5°.

II (1.00 g., 6.5×10^{-3} mole, m.p. 99–102°) and 3.25*M* aqueous sodium hydroxide (2.0 ml., 6.5×10^{-3} mole) were refluxed for 3.0 hr.; the solution was cooled and acidified with concentrated hydrochloric acid (0.5 ml.) to *p*H 2. There was no gas evolution. Refrigeration and filtration gave 0.682 g., m.p. 100.5–101.5°; mixed m.p. with starting material, m.p. 99–101°.

II (1.00 g., m.p. 99–101°) was refluxed with 2.0 ml. of 5% aqueous hydrochloric acid for 3.0 hr. Refrigeration and filtration gave 0.564 g., m.p. 99–103°; mixed m.p. with starting material, 99–103°.

II (1.00 g., m.p. 99–101°) was refluxed with 2.0 ml. ethyl acetate for 3.4 hr. Cooling at −20° and filtration gave 0.812 g., m.p. 99.5–101°; mixed m.p. with starting material, 99.5–101°.

A periodic acid test with II was negative.

endo-2-Carboxy-exo-3-carboxy-6-ketonorbornane (VI). A mixture of the lactone of *endo*-2-carboxy-*exo*-3-carboxy-*exo*-5-bromo-*endo*-6-hydroxynorbornane[10] (V) (26.1 g., 0.100 mole), sodium hydroxide (20.0 g., 0.500 mole) and water (400 ml.) was refluxed for 2.0 hr. After cooling to 25° concentrated hydrochloric acid (80 ml.) was added. After the solution was cooled again to 25° extraction with ethyl acetate (three 250-ml. portions) and evaporation of the combined extracts *in vacuo* at less than 70° gave fairly pure ketodicarboxylic acid VI, 16.5 g., 83% yield, m.p. 182.5–184° (reported[5] m.p. 186°).

Lactam of endo-2-carboxy-endo-6-aminonorbornane (III). Platinum oxide (0.200 g.) in water (60 ml.) was hydrogenated at 33 p.s.i. for 30 min.[11] The water was decanted from the platinum and to the platinum were added the keto acid (II) (2.00 g.) and concentrated aqueous ammonia (100 ml., density 0.90 g./ml.). The mixture was hydrogenated at about 50 p.s.i. and 48° for 24 hr. The metal tube which led gas into the hydrogenating bottle in the Parr hydrogenator was replaced with a glass inlet tube to avoid chemical reaction between the metal and ammonia. After removal of the catalyst by filtration the solution was evaporated at ⩽25° by a stream of air from an electric fan. The residual gum was dissolved in 5% sodium hydroxide (20 ml.) and the basic solution extracted with ether (six 50-ml. portions). The combined ether extracts were dried with sodium sulfate and evaporated *in vacuo*. The residue was heated *in vacuo* at 80° for 2 hr. Crystallization of the residual gum from a mixture of ether (3.0 ml.) and petroleum ether (6.5 ml., b.p. 30–75°) gave 0.610 g. (34%) of III, m.p. 152–154°. The crystallization must be done carefully,—*i.e.* slow cooling—to avoid oiling out. A portion of the collected product from two runs (1.105 g., m.p. 152–154°) was dissolved in ether (4.0 ml.) by stirring at room temperature. The addition of petroleum ether (10.0 ml., b.p. 30–75°) followed by standing successively at room temperature, 5° and finally −20° gave 0.962 g. of III, m.p. 153–154°. The lactam III was soluble in water and polar organic solvents. Infrared spectrum: (potassium bromide) 3.13, 3.25, and 5.95; (1% in chloroform) 2.93, 3.12, and 5.92 μ.

Anal. Calcd. for $C_8H_{11}NO$: C, 70.03; H, 8.08; N, 10.21. Found: C, 70.12; 7.86; N, 10.27.

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(10) K. Alder and G. Stein, *Ann.*, **504**, 216 (1933).

(11) Platinum oxide is reduced to platinum slowly, if at all, when hydrogenated in concentrated aqueous ammonia at room temperature and 1 to 3 atm. pressure. For similar findings see: (a) E. R. Alexander and A. L. Misegades, *J. Am. Chem. Soc.*, **70**, 1315 (1948); (b) A. C. Cope and E. M. Hancock, *J. Am. Chem. Soc.*, **64**, 1503 (1942).

Triphenyl Thioorthoborate

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Trimethyl thioorthoborate was first prepared by Goubeau and Wittmeier[1] by refluxing boron tribromide with an excess of silver or lead mercaptide; tri-*n*-butyl thioorthoborate has been prepared in like manner.[2] The method has been modified by Burg and Wagner[3] who found that sodium mercaptide could be used without a solvent. They also prepared the compound by heating polymeric thiomethoxyborine $(CH_3SBH_2)_x$. The alkyl thioorthoborates cannot be prepared by the corresponding procedures used for the oxygen analogs, such as by treating mercaptans with boron halides[1,4] nor could they be obtained from the action of boron halides on alkyl sulfides.[1,5]

In view of the unusual preparative methods required for the alkyl thioorthoborates, it was of some interest to find that thiophenol reacts smoothly with boron trichloride in boiling benzene to give, in good yield, the hitherto unknown triphenyl thioorthoborate. Phenol, in contrast, reacts readily at −80°.[6]

Triphenyl thioorthoborate is very similar to its oxygen analog, triphenyl orthoborate, except that it is much more difficult to obtain in a pure state. Both compounds are thermally stable, have similar melting and boiling points, and are extremely readily hydrolyzed in moist air.

EXPERIMENTAL

Thiophenol (70 g., 0.634 mole) was dissolved in 175 ml. of benzene, and a solution of 24.8 g. (0.211 mole) of boron trichloride in 75 ml. of benzene was added with stirring, in a dry nitrogen atmosphere. There was no noticeable heat evolution. The mixture was refluxed for 8 hr., after which time approximately one half the benzene was removed by distillation and the mixture allowed to cool. The white crystals which deposited were filtered in a dry box, washed with benzene, and dried with suction. Five successive crops afforded a total of 66.6 g. of the crude borate, representing a 93% yield. Difficulty was experienced in obtaining a pure specimen because benzene is readily incorporated by the crystals. Even after two recrystallizations from benzene the product did not melt sharply. Vacuum distillation of this purified material was attempted. The ester boiled at 193–194°/0.02 mm, but did not distill smoothly owing to solidification in the head and condenser. The liquid found in the liquid nitrogen trap protecting the pump proved to be mainly benzene.

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(1) J. Goubeau and H. W. Wittmeier, *Z. anorg. allgem. Chem.*, **270**, 16 (1952).

(2) M. F. Lappert, *Chem. Revs.*, **58**, 1106 (1958).

(3) A. B. Burg and R. I. Wagner, *J. Am. Chem. Soc.*, **76**, 3307 (1954).

(4) E. Wiberg and W. Sutterlin, *Z. anorg. allgem. Chem.*, **202**, 44 (1931).

(5) M. F. Lappert, *J. Chem. Soc.*, 2784 (1953).

(6) E. Wiberg and W. Sutterlin, *Z. anorg. allgem. Chem.*, **202**, 1 (1931).

Crystals recovered from the distillation head, m.p. (sealed tube) 129–143°, were analyzed by dissolving in 50% v./v. aqueous ethanol and titrating with $0.1N$ sodium hydroxide to the phenolphthalein end point, to determine the thiophenyl content. Mannitol was added and the boron content estimated by again titrating with sodium hydroxide to the phenolphthalein end point.

Anal. Calcd. for $C_{18}H_{15}BS_3$: B, 3.20; C_6H_5S, 96.8. Found: B, 3.09; C_6H_5S, 96.2.

The infrared absorption spectrum, determined with 10% w./v. solutions in carbon tetrachloride and carbon disulfide, exhibited peaks at the following wave numbers (cm.$^{-1}$): 685vs, 697vs, 740vs, 897vs, 916vs, 947s (broad), 1001w, 1024m, 1066m, 1093w, 1443s, 1452s, 1484s, 1587s, 3030m.

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Intramolecular Hydrogen Bonding to Sulfur

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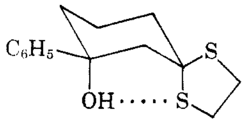
Although sulfur has not been well recognized as a base participating in hydrogen bonding, several reports have appeared implicating this atom as a proton acceptor.[1] Intermolecular hydrogen bonding between methanol and di-*n*-butyl sulfide was shown to give a shift of 155 cm.$^{-1}$ which was of the same magnitude as the shift found when oxygen was the proton acceptor in di-*n*-butyl ether.[2] This indicated that a high electronegativity was not the predominating factor in determining the hydrogen bonding ability of a base.[3] Evidence for intramolecular hydrogen bonding involving sulfur has been reported in 2,2′-thiodiphenol.[4] In this example the authors noted a decrease in frequency of a 149 cm.$^{-1}$ which is comparable to that found in intermolecular hydrogen bonding between methanol and di-*n*-butyl sulfide.

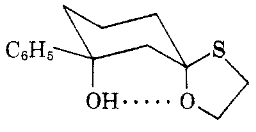
An example of intramolecular hydrogen bonding involving sulfur was examined in 7-phenyl-1,4-dithiospiro[4.5]-7-decanol (I). The evidence was derived from the absorption characteristics of I, 7-phenyl-1,4-oxathiospiro[4.5]-7-decanol (II), and 7-phenyl-1,4-dioxaspiro[4.5]-7-decanol (III) in the fundamental O—H stretching region and the first overtone in the near infrared. For additional verification of the assigned absorption peaks 8-phenyl-1,4-dioxaspiro[4.5]-8-decanol (IV) was examined.

Compound IV being a 1,4 system would have to assume the boat conformation prior to formation of intramolecular hydrogen bonding. Stolow[5] has demonstrated the existence of such bonding in a *cis*-1,4-cyclohexanediol forced into a twist conformation by interaction with *t*-butyl groups in positions 2 and 5. No evidence for intramolecular hydrogen bonding was found in IV. Two concentration-dependent peaks were found; one at 3604 cm.$^{-1}$ increased on dilution in nonpolar solvent and is assigned to unassociated hydroxyl.[6] Intermolecular hydrogen bonding was evident from a broad band at 3449 cm.$^{-1}$ which disappeared on dilution.

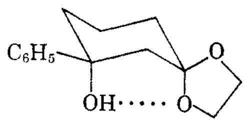
As expected compound III had a concentration independent band at 3503 cm.$^{-1}$, a shift of 101 cm.$^{-1}$ from the unassociated hydroxyl in IV. The magnitude of the shift, an increase of 26 cm.$^{-1}$ over that reported for *cis*-1,3-cyclohexanediol[7] indicates a stronger hydrogen bond which arises from the restriction of the hydroxyl and ether oxygen thereby decreasing the O......O distance.



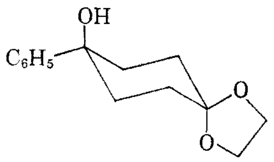
I



II



III



IV

The thioketal I showed two concentration independent bands, one at 3581 cm.$^{-1}$ and the other at 3446 cm.$^{-1}$ The former is a shift of 23 cm.$^{-1}$ indicating a weak bond. This spectral shift is in agreement with that reported for OH....π bonding.[8] The peak of 3446 cm.$^{-1}$ is a shift of 158 cm.$^{-1}$ from the position assigned for unassociated hydroxyl. This indicated a slightly stronger bond than that reported for 2,2′-thiodiphenol.[4]

The determination of the conformation of the hemithioketal was made by comparison of models of compounds I, II, and III and their absorption in the hydroxyl stretching region. Measurements made on stereo models indicate that if II has both oxygens *cis*, the O.....O distance is slightly greater than found in III due to the sulfur and the corresponding increase in bond lengths in the oxathiolane ring. Thus, the spectral shift should be less than 101 cm.$^{-1}$ found in III. Similarly if

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