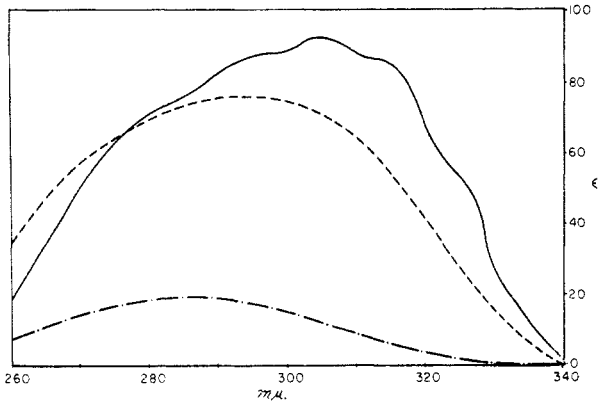


Fig. 1. Ultraviolet absorption spectra of 3,3-dimethyl-2,4-pentanedione in petroleum ether (b.p. 69–96°) (———); 3,3-dimethyl-2,4-pentanedione in absolute ethanol (– – – –); and methyl *tert*-butyl ketone in petroleum ether (b.p. 69–96°) (-·-·-·)

solvent polarity on the relative concentrations of C and D is consistent with the results obtained with α-bromocyclohexanones.[7b]

The ultraviolet spectra of I in both hydrocarbon and ethanol solvents (Fig. 1) are considerably different from that expected of a compound with a pair of isolated carbonyl groups (*cf.* methyl *tert*-butyl ketone, Fig. 1). In hydrocarbon solvent there is a maximum at 305 mμ (ε 93) and four shoulders—a spectrum that is more complex than that for the normal n → π* transition of simple ketones. With ethanol as solvent the maximum is shifted to lower wave length. This is the usual "blue shift" observed with solvents capable of hydrogen bonding with the carbonyl chromophore.[9]

The presence of an axial α-halogen is known to cause a bathochromic shift in $\lambda_{max}$ and an increase of the extinction coefficient in the ultraviolet spectra of cyclic ketones.[10] Application of this result to the present case suggests that conformation D is mainly responsible for the observed anomalous ultraviolet absorption. It has been suggested that the shifts observed with axial α-halo ketones are due to hyperconjugation.[10b] While this may also be true with D, another interpretation is that overlap between the p-orbitals on the carbonyl carbons occurs and, in fact, the geometry of D is favorable for this type of overlap. A similar explanation has been used to account for the spectral abnormalities of phenyl and benzyl acetone.[11] In any event, interpretation of the electronic spectra is subject to the usual difficulties in deciding whether a shift in $\lambda_{max}$ is the result of a change in the ground state or the excited state.

(9) G. J. Brealy and M. Kasha, *J. Am. Chem. Soc.*, **77**, 4462 (1955).

(10) (a) R. C. Cookson, *J. Chem. Soc.*, 282 (1954); (b) E. J. Corey and H. J. Burke, *J. Am. Chem. Soc.*, **77**, 5418 (1955).

(11) R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, 2303 (1956); S. F. Marsocci and S. MacKenzie, *J. Am. Chem. Soc.*, **81**, 4513 (1959).

## EXPERIMENTAL

3,3-Dimethyl-2,4-pentanedione was prepared essentially by the published method[12] through stepwise dimethylation of acetylacetone. Considerable difficulty was experienced in introducing the second methyl group until it was discovered that reducing the reaction time to 20 min. prior to removal of the ethanol by distillation gave the product in 65–70% yield. Purification by fractional distillation followed by extraction with aqueous cupric acetate yielded material contaminated with 1.5% monomethyl acetylacetone (analysis by gas-liquid chromatography[13]). Low temperature recrystallization from pentane reduced the impurity to < 0.1%.

Infrared spectra were determined on a Beckman IR-5 instrument[14] with an estimated accuracy of ±0.01 μ (± 3 $cm.^{-1}$). Each spectrum was calibrated with the 6.24-μ (1602 $cm.^{-1}$) polystyrene band. Ultraviolet spectra were measured on a Beckman DK-2 spectrophotometer.[15] All solvents used for solution spectra were purified.

Department of Chemistry
Colorado State University
Fort Collins, Colo.

(12) R. G. Pearson and E. A. Mayerle, *J. Am. Chem. Soc.*, **73**, 926 (1951).

(13) Separation of acetylacetone from its mono- and dimethylated derivatives was achieved by use of a 10-ft. poly(diethyleneglycol succinate) column operated at 145° with a helium flow rate of 50 ml./min. The compounds emerge in the reverse order of increasing molecular weight.

(14) Purchased with funds from National Science Foundation grant NSF-G16358 for which acknowledgment is gratefully made.

(15) We wish to thank Mr. Wilbert Shimoda for the ultraviolet measurements.

## Synthesis of *endo*-2-Carboxy-*endo*-6-aminonorbornane Lactam[1]

Richard W. Iles and W. Scott Worrall

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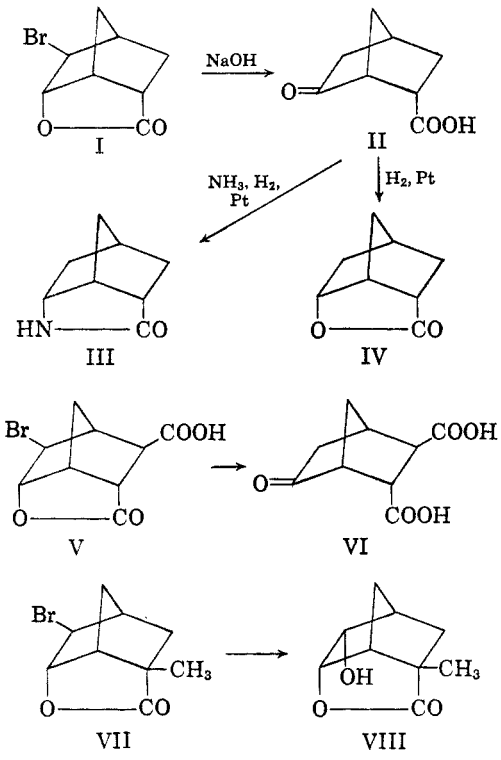
The synthesis of the lactam of *endo*-2-carboxy-*endo*-6-aminonorbornane (III) was of interest because a knowledge of the properties of the monolactam is potentially useful for the solution of the intimate structure of the dilactam of *endo-cis*-2,3-dicarboxy-*endo-cis*-5,6-diaminonorbornane.[2] In the dilactam it is not known whether both the lactam groups are in the usual keto form or whether one of the lactam groups is in the unusual enol form. The lactone of *endo*-2-carboxy-*exo*-5-bromo-*endo*-6-hydroxynorbornane[3] (I) with aqueous sodium hydroxide at room temperature gave *endo*-2-carboxy-6-ketonorbornane (II). Evidence for the structure of the keto acid II is: the elemental analysis; the infrared spectrum, 5.7 μ for the ketone and 5.85

(1) This work was supported by a research grant, G-11381, from the National Science Foundation.

(2) W. S. Worrall, *J. Am. Chem. Soc.*, **82**, 5707 (1960).

(3) C. D. Ver Nooy and C. S. Rondestvedt, Jr., *J. Am. Chem. Soc.*, **77**, 3583 (1955).




$\mu$ for the carboxyl; the uptake of one mole of hydrogen on catalytic hydrogenation; the *endo* position of the carboxyl group as indicated by the fact that the product of hydrogenation was the known lactone of *endo* 2 carboxy-*endo*-6-hydroxynorbornane[4] (IV). The reaction is modeled after the original reaction of Alder and Stein[5] in which the lactone of *endo*-2-carboxy - *exo* - 3 - carboxy - *exo* - 5 - bromo - *endo*-6-hydroxynorbornane (V) was converted to *endo*-2-carboxy - *exo* - 3 - carboxy - 6 - ketonorbornane[6] (VI). It is interesting that Meek and Trapp[7] found that basic treatment of the bromolactone (and also the iodolactone) followed a different reaction route when the *exo*-2 group is a methyl rather than a hydrogen—*i.e.*, the lactone of *exo*-2 - methyl - *endo* - 2 - carboxy - *exo* - 5 - bromo-*endo*-6-hydroxynorbornane (VII) gave the 2,6-lactone of *exo*-2-methyl-*endo*-2-carboxy-*endo*-5,6-dihydroxynorbornane (VIII). The ease of decarboxylation of the keto acid II was also of interest because of the possibility of orbital overlap between the 2- and 6- positions with a consequent participation of the 6-keto group. However, the keto acid II was stable when refluxed either in dilute aqueous acid or in dilute aqueous base. Reductive alkylation[8] with the keto acid II gave the lactam III directly. Evidence for the structure of the lactam III is: the elemental analysis; the method of synthesis; and the infrared spectrum which is the same as that reported for cyclic lactams both in the condensed phase and in chloroform solution and both in the N—H stretching region and in the carbonyl region.[9]

(4) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett, and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3116 (1950).

(5) K. Alder and G. Stein, *Ann.*, **525**, 183 (1936).

(6) An improved procedure for this particular reaction is given in the Experimental section.

(7) J. S. Meek and W. B. Trapp, *J. Am. Chem. Soc.*, **79**, 3909 (1957).

(8) W. S. Emerson, *Org. Reactions*, 174 (1948).

## EXPERIMENTAL

*endo-2-Carboxy-6-ketonorbornane* (II). The lactone of *endo*-2-carboxy-*exo*-5-bromo-*endo*-6-hydroxynorbornane[3] (I) (21.7 g., 0.100 mole) was added to a solution of sodium hydroxide (16.0 g., 0.40 mole) in water (300 ml.) at 25° and the mixture stirred for 60 min. with no external heating or cooling. The temperature rose to about 29°. Concentrated hydrochloric acid (25 ml.) was added with cooling so that the temperature remained $\leq$25°. A trace of coagulated insoluble gum was removed by filtration. The filtrate in a large evaporating dish was evaporated at $\leq$25° by a stream of air from an electric fan. The evaporating solution was stirred continually to prevent the formation of a surface crust. The residual mushy crystals were extracted with three 50-ml. portions of chloroform and the combined chloroform extracts were evaporated *in vacuo* at less than 25°. The partly crystalline residue was swirled with ethyl acetate (30 ml.); the resulting suspension was cooled at −20° overnight and filtered to give 7.1 g. of crude product (II). Recrystallization from ethyl acetate (14 ml.) gave 6.0 g. of II, m.p. 98.5–101°. An additional 1.5 g. of II, m.p. 98–100°, was obtained by working up the original ethyl acetate filtrate followed by recrystallization from ethyl acetate; total yield, 49%. The analytical sample, m.p. 101.5–103.5°, was obtained by several additional recrystallizations from ethyl acetate and drying *in vacuo* for 24 hr. at room temperature. At room temperature the keto acid II was fairly soluble in water, ethyl acetate, and chloroform and insoluble in benzene and carbon tetrachloride. Infrared spectrum: (1% in chloroform) 5.7 and 5.85 $\mu$.

*Anal.* Calcd. for $C_8H_{10}O_3$: C, 62.31; H, 6.54. Found: C, 62.54; H, 6.66.

*Conversion of the keto acid* II *to the lactone of endo-2-carboxy-endo-6-hydroxynorbornane* (IV). A mixture of the keto acid II (0.400 g., 2.60 mmoles), water (25 ml.), and concentrated hydrochloric acid (0.2 ml.) was stirred with hydrogen at room temperature and 1 atm. in the presence of prereduced platinum oxide (0.100 g.) for 24 hr. At the end of this period 73 ml. of hydrogen had been taken up and the adsorption had stopped. Because of the fluctuation of the room temperature and the barometric pressure the theoretical uptake was not calculated. Assuming a room temperature of 23° and a pressure of 760 mm. the theoretical uptake would be 65 ml. After removal of the catalyst by filtration the aqueous solution was extracted with ether (two 20-ml. portions) and the combined ether extracts were evaporated *in vacuo* at $\leq$room temperature. The residue was dried in a Drierite desiccator for several days to give a glass. Two recrystallizations from pentane gave 0.134 g. (37%) of the lactone IV, m.p. 152–154.5°. A mixed melting point of this material with lactone prepared as reported in the literature[4] was undepressed and the infrared spectra (1% in chloroform) of the two materials were identical.

*Properties of endo-2-carboxy-6-ketonorbornane* (II). II (1.00 g., m.p. 99–101°) was dissolved in water (2.0 ml.) by heating to boiling. The resulting solution was cooled at once and refrigerated for 2 days. Filtration gave 0.503 g., m.p. 100.5–102°. This procedure was repeated except that

(9) L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, Wiley, New York, 1958, p. 206, 214, 217.

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., $6.5 \times 10^{-3}$ mole, m.p. 99–102°) and 3.25*M* aqueous sodium hydroxide (2.0 ml., $6.5 \times 10^{-3}$ 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.

Department of Chemistry
Trinity College
Hartford, Conn.

(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

D. M. Young and C. D. Anderson

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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.

(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).