75°. One mole of dibromoalkane (or 2 moles of alkyl bromide for the preparation of monothiols) was added. The mixture was stirred until it became homogeneous. The temperature was kept below 130°. After an additional 15 min. of stirring, a vacuum pump was attached to the system. Tetraethylenepentamine (189.3 g.; 1 mole) was added at a rate which prevented foaming or too rapid reaction. Heat was applied and total reflux continued until the head temperature became constant. Distillation was then begun and the product collected.

*Reaction of morpholine with ethane-1,2-bisisothiuronium bromide.* One mole (340 g.) of ethane-1,2-bisisothiuronium bromide was mixed with 4 moles (348.5 g.) of morpholine in a flask equipped with a stirrer, a thermometer, and an efficient condenser. The exothermic reaction raised the temperature to 90°. The viscous solution was heated on a steam bath and stirred for 18 hr. It was cooled and poured into 1 l. of rapidly stirred benzene. A crystalline product separated. It was completely water-soluble. The benzene layer was separated and distilled. 2-Morpholinoethanethiol, 92.5 g. (63%), b.p. 93°/12 mm., $n_{\mathrm{D}}^{25}$ 1.5028 (lit.[8] b.p. 83°/11 mm., $n_{\mathrm{D}}^{25}$ 1.5000), was collected. It was 98.5% pure, as shown by iodometric titration.

*Reaction of di-n-butylamine with ethane-1,2-bisisothiuronium bromide.* One mole (340 g.) of ethane-1,2-bisisothiuronium bromide was stirred into 4 moles of di-*n*-butylamine. There was no apparent heat of reaction. This mixture was stirred under a reflux condenser for 18 hr. at 90°. The resulting white slurry was cooled and added to 1 l. of rapidly stirred benzene. One liter of water was added and stirring continued for 10 min. The mixture was filtered by suction. The benzene layer from the filtrate was separated and distilled to yield 42 g. (22.2%) of 2-di-*n*-butylaminoethanethiol (b.p. 99°/8 mm.; $n_{\mathrm{D}}^{25}$ 1.4632) (lit.[5] b.p. 66°/0.7 mm.; $n_{\mathrm{D}}^{25}$ 1.4622) and 23 g. of higher-boiling residue. The insoluble residue which remained on the funnel was dried to yield 33 g. of a polyethylene sulfide. This was dissolved in hot dimethyl sulfoxide, filtered, cooled, and stirred into 500 ml. of benzene. The white product was then extracted in a Soxhlet extractor with benzene and dried.

Elemental analysis, iodometric titration, and infrared spectra indicate that this is a polymer having the structure $(n\text{-}C_4H_9)_2N(CH_2CH_2S)_nH$.

*General preparative procedure for 1,2-ethanedithiol using ammonium hydrosulfide.* A 2-l., three necked, round bottomed flask, immersed in an ice-salt bath, was fitted with a stirrer, a gas inlet tube extending below the surface of the liquid, and a connecting tube with a parallel sidearm fitted with a thermometer and an addition funnel.

In the flask were placed 350 ml. of methanol and 350 ml. (4.6 moles) of concd. ammonium hydroxide. The solution was cooled to −5° and saturated with hydrogen sulfide at −5° to +5°. While hydrogen sulfide continued to pass slowly into the solution, 2 moles of the mercaptoethylating agent was added in small portions over a 30-min. period. During the addition, the temperature was maintained at 5–10°. Hydrogen sulfide was passed into the mixture for 2 hr. after the addition was complete. The mixture was stirred for 20 hr. at 25–30°.

The mixture was cooled to 0° and made acid to Congo red paper with concentrated hydrochloric acid. The product was extracted with four 250-ml. portions of chloroform, which were combined and dried over anhydrous magnesium sulfate. After filtration, the chloroform was removed by distillation. The reaction product was distilled through a 2.5 × 16-cm. column packed with glass helices, at reduced pressure, using a Dry Ice trap. When the mercaptoethylating agent was ethyl 2-mercaptoethylcarbonate (VI), 1,2-ethanedithiol was obtained in 70–80% yields. B.p. 73°/62 mm.; $n_{\mathrm{D}}^{25}$ 1.5562.

*Anal.* Calcd. for $C_2H_6S_2$: C, 25.5; H, 6.4; S, 68.1. Found: C, 25.4; H, 6.2; S, 68.3.

ROCHESTER, N. Y.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, VIRGINIA POLYTECHNIC INSTITUTE]

# Unsaturated Cyclic Sulfones. V. 3-Methyl-2,3-dihydrothiophene 1,1-Dioxide

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The synthesis of 3-methyl-2,3-dihydrothiophene 1,1-dioxide is described, and the base-catalyzed isomerization of this compound gave 18% 3-methyl-4,5-dihydrothiophene 1,1-dioxide, and 55% 4-hydroxy-3-methyltetrahydrothiophene 1,1-dioxide.

Of the three 3-methyldihydrothiophene 1,1-dioxides only the 2,3-dihydro isomer was unknown. Böeseken and van Zuydewijn[2] suggested that the action of an aqueous solution of potassium hydroxide on 3-methyl-2,5-dihydrothiophene 1,1-dioxide (I) should give rise to the 2,3-dihydro (VI) and the 4,5-dihydro isomers (VII); however, only VII was isolated. Ozonolysis of the reaction product and the analysis of the resulting sulfonic acids indeed indicated that a very small amount of VI was probably in the product. Thus, the isomerization of I as a synthetic route to VI did not appear attractive.

The synthesis of VI *via* 4-hydroxy-3-methyltetrahydrothiophene 1,1-dioxide (II) from I appeared to be particularly attractive using the novel hydroboration technique of Brown and Subba Rao.[3] The hydroboration of I at 0° was not successful; however, the initiation of reaction at room temperature with subsequent control of the temperature between 25–50° during reaction gave II in 63% yield. The structure of II was confirmed as shown in the formula sequence compounds I → VII.

The oxime (III) and the unsaturated ketone (IV) were reported previously,[4] and the reduction of IV gave II.

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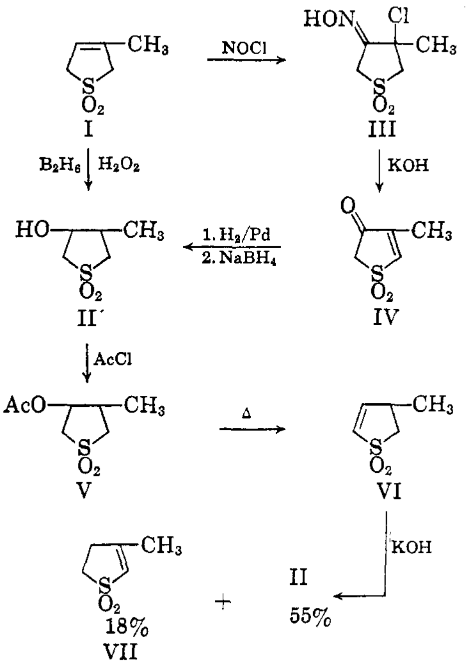
[1] Taken from the M.S. thesis of Donald E. Boswell, November 1960.

[2] J. Böeseken and E. de Roy van Zuydewijn, *Proc. Acad. (Amsterdam)*, **37**, 760 (1934).

[3] H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **81**, 6423, 6428 (1959).

[4] R. C. Krug, G. R. Tichelaar, and F. E. Didot, *J. Org. Chem.*, **23**, 212 (1958).



Although the dehydration of II should lead to VI, preliminary studies indicated that the other avenues of attack might prove to be more fruitful.

Dehydrohalogenation of certain compounds has been shown to be a practical route to the introduction of a double bond. Thus, II was converted to the corresponding chloride[5] using thionyl chloride. The action of ethanolic potassium hydroxide on the chloride gave evidence of the formation of I, VI, and VII. Pyridine did not effect dehydrochlorination, and the chloride was recovered.

The acetate (V) from II was prepared in 78% yield with the use of acetyl chloride in chloroform. Pyrolysis of the acetate at 475–485° gave III in 52% yield. This isomer (VI) was the only one of the three position isomers which was a liquid. As is generally true with similar liquid sulfones, VI decomposed very slowly upon standing at room temperature.

The structure of VI was established by catalytic reduction to 3-methyltetrahydrothiophene 1,1-dioxide. The infrared spectrum of VI (the only isomer having a *cis*-disubstituted carbon-carbon double bond) supports the assigned structure.

As expected VI reacts with bromine and the adduct was obtained in 73% yield. Surprisingly, the crude dibromide had a sharp melting point in distinct contrast to the result found with 2-methyl-2,3-dihydrothiophene 1,1-dioxide.[6] Perhaps the methyl group in the 3-position effects such steric control that the bromine adduct of VI is a simple racemic mixture and not the two pairs of racemates expected, assuming *trans* addition to the double bond.

The treatment of VI with an alcoholic solution of potassium hydroxide for four days at room temperature gave 18% of VII and a 55% crude yield of II. There was no evidence of the presence of I in the reaction product.

## EXPERIMENTAL[7]

*3-Methyl-2,5-dihydrothiophene 1,1-dioxide* (I). A modification of the procedure of Frank and Seven[8] was used; however, the purification of I did not require the use of Norit. Impure I was recrystallized from methanol, washed once with petroleum ether (b.p. 30–60°) and dried in a vacuum desiccator to give white, flaky crystals, m.p. 63–64°, 81% yield.

*4-Hydroxy-3-methyltetrahydrothiophene 1,1-dioxide* (II). The reaction flask was a 1000-ml. three-neck flask equipped with a diborane inlet tube, thermometer, diborane outlet, and magnetic stirrer. In the reaction flask was placed 119 g. (0.90 mole) of I dissolved in 420 ml. of freshly distilled anhydrous tetrahydrofuran. In the pressure equilibrated dropping funnel of the diborane generator was placed a solution of 25.7 g. (0.68 mole) of sodium borohydride in 555 ml. of bis(2-methoxyethyl) ether (freshly distilled from sodium, b.p. 158–161°). In the flask of the generator was placed a solution of 130 g. (0.92 mole) of boron trifluoride etherate (freshly distilled, b.p. 124–126°) in 200 ml. of bis(2-methoxyethyl) ether. The reaction flask containing the sulfone was immersed in a water bath at room temperature and slow stirring was initiated in the system. The generator and reaction flask were flushed with nitrogen for 15 min. The nitrogen flow was reduced almost to zero and the sodium borohydride solution was added slowly to the generator flask over a period of 3 hr. The temperature in the reaction flask would rise to approximately 50° during the addition period. When the addition was complete, the nitrogen flow was continued for 2 hr. or until the reaction mixture had cooled to room temperature. The water bath was replaced with an ice-salt bath and the inlet tube of the reaction flask was replaced with a pressure equalized dropping funnel in order to carry out the oxidation *in situ*. When the reaction mixture had cooled to 0°, water was added slowly until hydrogen evolution had ceased. Now 202 ml. of 3*N* sodium hydroxide was added dropwise so that the temperature of the reaction mixture did not exceed 20°, followed by the addition of 135 ml. of 30% hydrogen peroxide solution under the same conditions. The upper layer of the reaction mixture was separated and extracted with five 100-ml. portions of ether. The ether extracts were combined and dried over magnesium sulfate. The mixture was filtered and the solvent was removed under vacuum to give 85 g. (63%) of crude II, m.p. 62–64°. Pure II was obtained by crystallization of distilled II (b.p. 163–164°/0.035 mm.) from a mixture of tetrahydrofuran and petroleum ether (b.p. 35–50°) using a standard solvent-pair technique,[9] m.p. 63–64°.

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[5] Recently we found that this chloride had been prepared by the oxidation of the corresponding sulfide; F. E. Brown, *Synthesis and Chemistry of Di and Tetrahydrothiophenes*," Tulane University, *Diss. Abs.*, **21**, 2106 (1961). No physical constants were given in the abstract.

[6] R. C. Krug and J. A. Rigney, *J. Org. Chem.*, **23**, 1697 (1958).

[7] All melting points and boiling points are in degrees centigrade and uncorrected. The quantitative analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn. Infrared spectra were obtained using a Beckman IR-5 spectrophotometer. Anhydrous sulfur dioxide was supplied through the courtesy of the Virginia Smelting Co., West Norfolk, Va., and the Enjay Chemical Co., Elizabeth, N. J., kindly supplied the 2-methyl-1,3-butadiene.

[8] R. L. Frank and R. P. Seven, *Org. Syn.*, **Coll. Vol. III**, 499 (1955).

[9] A. I. Vogel, *Practical Organic Chemistry*, Longmans, Green & Co., New York, 1948, p. 124.

For preparative purposes, it was adequate to recrystallize II from the minimum amount of tetrahydrofuran by refrigeration.

*Anal.* Calcd. for $C_5H_{10}O_3S$: C, 39.98; H, 6.71; S, 21.35. Found: C, 40.19; H, 6.75; S, 21.47.

The infrared spectrum of II (0.52% in potassium bromide wafer) showed the following principal frequencies: 3497, 3012, 2967, 1637, 1464, 1410, 1295, 1248, 1208, 1149, 1124, 1012, 978, 907, 820, 647 cm.$^{-1}$

*3-Chloro-4-oxo-3-methyltetrahydrothiophene 1,1-dioxide oxime.* (III). The procedure employed was essentially that which was reported earlier[4] except for the fact that reagents and solvents were not purified. Purification of reagents and solvent appeared to inhibit the onset of reaction. The product was recrystallized from ethanol to give III, m.p. 148–150°, 55% yield.

*3-Oxo-4-methyl-2,3-dihydrothiophene 1,1-dioxide* (IV). A modification of the earlier procedure[4] was used. Volatile matter was removed under vacuum from the reaction mixture. The residue was evaporated to dryness on the steam bath and crude IV was extracted from the salt mass with anhydrous acetone. The red solution was treated with Norit to give a partial clarification. Evaporation of the acetone and two recrystallizations from ethanol gave 2.6 g. (22%) of IV, m.p. 164–165°.

*4-Hydroxy-3-methyltetrahydrothiophene 1,1-dioxide.* To 50 ml. of chloroform were added 1 g. (0.007 mole) of IV and 0.1 g. of 10% palladium on carbon catalyst. The mixture was treated with hydrogen in a Parr hydrogenation apparatus (Parr Instrument Co., Item No. 3911) for 25 min. at 40.5 p.s.i. No pressure drop was noted. Upon filtering the solution and evaporating the solvent, approximately 1.0 g. of a white solid remained, m.p. 140–143°. This uncharacterized solid was dissolved in 75 ml. methanol and treated with a solution of 0.11 g. of sodium borohydride in 13 ml. of water. The reaction mixture was warmed to 45–50° for 45 min. and 3 drops of concd. hydrochloric acid was added. After removing the solvents under vacuum, a syrupy residue remained. This residue resisted conventional attempts at crystallization and was subsequently chilled in Dry Ice. Solid particles which appeared in the solution were quickly removed and leached of the mother liquor on filter paper. This solid gave a positive ceric ammonium nitrate test and gave no depression in a mixed melting point test with II, m.p. 62–64°.

*4-Chloro-3-methyltetrahydrothiophene 1,1-dioxide.* A solution of 3.4 g. (0.02 mole) of II in 26 ml. of chloroform was placed in a 50-ml. flask equipped with a reflux condenser and drying tube. One drop of pyridine and 4.7 g. (0.04 mole) of freshly distilled thionyl chloride were added rapidly at room temperature. The solution was heated to reflux for 51 hr. and the volatile portion was then removed under vacuum. The oily residue was dissolved in a small volume of ethanol and refrigerated to deposit crystals overnight. Recrystallization from absolute ethanol gave diamond shaped plates, 3 g. (81%) m.p. 92–93°.

*Anal.* Calcd. for $C_5H_9ClO_2S$: C, 35.61; H, 5.38; Cl, 21.02; S, 19.01. Found: C, 35.32; H, 5.29; Cl, 21.20; S, 19.24.

The infrared spectrum of the chloride (0.49% in potassium bromide wafer) showed the following principal frequencies: 3012, 1466, 1406, 1318, 1284, 1253, 1232, 1163, 1147, 1096, 1000, 938, 917, 842, 789, 712, 647 cm.$^{-1}$

*Dehydrochlorination of 4-chloro-3-methyltetrahydrothiophene 1,1-dioxide.* Ten grams (0.06 mole) of the chloride was dissolved in 35 ml. of ethanol and placed in a 200-ml. three-neck flask equipped with a magnetic stirrer, reflux condenser, dropping funnel, and thermometer. The mixture was brought to reflux and a solution of 3.9 g. (0.06 mole) of 86.7% pure potassium hydroxide in 69 ml. of ethanol was added. The solution was cooled to room temperature and neutralized with 6*N* hydrochloric acid, chilled, filtered, and the volatile portion was removed under vacuum. The oily residue was distilled with decomposition (sulfur dioxide evolved) to give 1.5 g. of an oil, b.p. 133–134°/0.1–2.0 mm., whose infrared spectrum indicated the presence of I, VI, VII, and an ethoxy compound.

*4-Acetoxy-3-methyltetrahydrothiophene 1,1-dioxide* (V). A solution of 18.2 g. (0.12 mole) of II in 50 ml. of chloroform was placed in a 200-ml. three-neck flask equipped with a reflux condenser, drying tube, magnetic stirrer, and dropping funnel. The reaction mixture was chilled in an ice bath and 28.2 g. (0.36 mole) of acetyl chloride was added over 1 hr. with stirring. The mixture was allowed to warm to room temperature and was heated to reflux for 4 hr. The volatile matter was removed under vacuum and the residue was distilled to give 18.0 g. (78%) of V, b.p. 135–137°/0.1 mm., $n_D^{20}$ = 1.4757, $d_{20}^{20}$ = 1.2686.

*Anal.* Calcd. for $C_7H_{12}O_4S$: C, 43.74; H, 6.29; S, 16.68. Found: C, 44.43; H, 6.29; S, 17.51.

The infrared spectrum of V (10 vol. % in benzene) showed the following principal frequencies: 3003, 1748, 1408, 1376, 1318, 1227, 1134, 1046, 917, 818, 636 cm.$^{-1}$.

*3-Methyl-2,3-dihydrothiophene 1,1-dioxide* (VI). The pyrolysis tube was packed for 6″ in the furnace zone with Pyrex wool covered by 1 in. of glass beads (5 mm. diameter). An iron-constantan thermocouple was inserted into the center of the packing. To the top of the tube was connected a pressure equilibrated dropping funnel, and a 6-in. double-surface condenser was attached to the exit end of the tube.

A solution of 22.3 g. (0.12 mole) of V in 53 ml. of anhydrous benzene was introduced into the tube at a rate of 25 drops per minute under a low flow of nitrogen. The contact zone was maintained at 475–485°. At the end of the addition, the system was flushed with 5 ml. of acetone. The pyrolysate was dark and clear. Removal of the solvents under vacuum and distillation of the residue gave 8 g. (52%) of III, b.p. 107–108°/0.5 mm., $n_D^{20}$ = 1.4620, $d_{20}^{20}$ = 1.1702.

*Anal.* Calcd. for $C_5H_8O_2S$: C, 45.43; H, 6.10; S, 24.26. Found: C, 45.63; H, 6.10; S, 23.90.

The infrared spectrum of VI(10 vol. % in benzene) showed the following principal frequencies: 2976, 1821, 1634, 1449, 1410, 1302, 1220, 1130, 1115, 1066, 938, 890, 856, 733, 632 cm.$^{-1}$

*3-Methyltetrahydrothiophene 1,1-dioxide.* In a Parr hydrogenation apparatus, 3 g. (0.02 mole) of VI in 14 ml. of ethanol was reduced with hydrogen (39.4 p.s.i.) in the presence of 0.1 g. of 10% palladium on carbon. The reaction mixture was filtered and the filtrate distilled in vacuum to give 2.5 g. (80%), b.p. 81–82°/0.1 mm., (lit.[10] b.p. 102–103°/2–3 mm.).

*2,3-Dibromo-4-methyltetrahydrothiophene 1,1-dioxide.* Into a small glass stoppered bottle was placed a solution of 3.8 g. (0.03 mole) of VI in 13 ml. of chloroform, 0.1 g. of aluminum chloride, and 4.8 g. (0.03 mole) of bromine. The stopper was sealed with wax and the mixture allowed to stand in light for 30 days. The solvent was removed under vacuum and the residue was treated with solid sodium bisulfite. Distillation of the residue gave 6 g. (73%) of crude dibromide, b.p. 160–163°/2.0–2.9 mm. Three recrystallizations from ethanol gave sturdy rods, m.p. 93.4–94°.

*Anal.* Calcd. for $C_5H_8Br_2O_2S$: C, 20.57; H, 2.76; Br, 54.73; S, 10.98. Found: C, 20.85; H, 3.03; Br, 54.57; S, 10.96.

The infrared spectrum of II (0.52% in potassium bromide wafer) showed the following principal frequencies: 3497, 3012, 2967, 1637, 1464, 1410, 1295, 1248, 1208, 1149, 1124, 1012, 978, 907, 820, 647 cm.$^{-1}$.

*Base-catalyzed isomerization of* VI. Six and six-tenths grams (0.05 mole) of VI was stirred with 135 ml. of 0.5*N* aqueous potassium hydroxide for 4 days at room temperature. The solution was then extracted with four 30-ml. portions of chloroform and the combined extracts were concentrated under vacuum. Recrystallization of the residue from ethanol gave 1.2 g. (18%) of II, m.p. 73–75°. No depression was found in a mixed melting point determination with an authentic sample of VII. The aqueous layer from

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[10] H. J. Backer and C. C. Bolt, *Rec. trav. chim.*, **54**, 538 (1935).

the isomerization mixture was neutralized with $6N$ hydrochloric acid and was evaporated to dryness on the steam bath. The solid mass was extracted with anhydrous acetone. The acetone was evaporated and the residue was distilled to give 4.2 g (56%) of crude II, b.p. 157–161°/0.1 mm., which showed a positive ceric ammonium nitrate test. No depression was found in a mixed melting point determination with an authentic sample of II.

BLACKSBURG, VA.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

# 4-Benzylidine-2,3-dioxopyrrolidines and 4-Benzyl-2,3-dioxopyrrolidines. Synthesis and Experiments on Reduction and Alkylation[1]

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The acid-catalyzed condensation of benzaldehyde with 1-substituted 2,3-dioxopyrrolidines (I) yielded 1-substituted 4-benzylidene-2,3-dioxopyrrolidines (III). A convenient preparative procedure is described in which 1-substituted 2,3-dioxopyrrolidines (I) are formed by acid hydrolysis and decarboxylation of the readily available 1-substituted 4-carbethoxy-2,3-dioxopyrrolidines (II) and condensed with benzaldehyde in a single operation. Sodium borohydride reduced both the conjugated olefinic bond and the ketonic carbonyl group of the 4-benzylidene derivatives (III) to yield 1-substituted 4-benzyl-3-hydroxy-2-oxopyrrolidines (XI). The latter compounds were reduced with lithium aluminum hydride to 1-substituted 4-benzyl-3-hydroxypyrrolidines (XII). Catalytic hydrogenation of the 4-benzylidene derivatives (III) yielded the 1-substituted 4-benzyl-2,3-dioxopyrrolidines (VIII). These highly enolized compounds [actually 1-substituted 4-benzyl-3-hydroxy-2-oxo-3-pyrrolines (IX)] resemble phenols in displaying appreciable acidity, forming deeply colored ferric chloride complexes and yielding ambident anions which undergo both C and O alkylation. Ketonic behavior was evident, however, in the formation of aniline derivatives (XV).

Simple 2,3-dioxopyrrolidines (I) with substituents only at the 1-position can be obtained conveniently by acid hydrolysis and decarboxylation of the readily available 1-substituted 4-carbethoxy-2,3-dioxopyrrolidines (II).[3] The dioxopyrrolidines (I) are promising starting materials for the synthesis of a variety of structures containing the pyrrolidine ring and have, for example, already been utilized for the synthesis of compounds related to the alkaloid vasicine.[4] The present investigation is concerned with the possibility of utilizing the 2,3-dioxopyrrolidines as the active methylene components in aldol condensations, in order to obtain additional types of pyrrolidine derivatives.

A pronounced tendency to undergo condensation reactions involving the methylene group at the 4-position was evident from earlier observations of the behavior of 2,3-dioxopyrrolidines; certain of these compounds had been found to undergo self-condensation in the aldol manner with remarkable speed under basic or even essentially neutral reaction conditions.[3a,5,6] However, the objective of the present investigation was to avert the self-condensations and permit the 2,3-dioxopyrrolidines to condense with the carbonyl function of other compounds. The objective has been achieved with benzaldehyde as the other carbonyl compound, and the resulting 4-benzylidene-2,3-dioxopyrrolidines (III) have been converted into a number of other types of substituted pyrrolidines, as discussed below.

The condensation of benzaldehyde with 2,3-dioxopyrrolidines was not achieved with a basic catalyst (pyridine); self-condensation of the 2,3-dioxopyrrolidine to the aldol condensation product (VII) occurred instead.[3a] The suppression of the self-condensation in favor of reaction with benzaldehyde was accomplished very successfully under acidic conditions, however. Evidently the enol form (IV) of the 2,3-dioxopyrrolidine is attacked more rapidly by protonated benzaldehyde (V) than by protonated 2,3-dioxopyrrolidine (VI), but it is uncertain whether the outcome reflects a higher intrinsic reactivity of V than of VI, or merely a lower concentration of VI. Actually, self condensation of the 2,3-pyrrolidinediones (I) does occur in acid solution, but only to a limited extent.[7] The enols IV, unlike many related compounds which have a substituent in the 4- position (*vide infra*), have not been isolated.

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(1) This investigation was supported by a research grant (RG-4371) from the National Institutes of Health, Public Health Service.

(2) This paper is based on a thesis submitted by Eugene F. Barnas in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Carnegie Institute of Technology, May 1960.

(3) (a) P. L. Southwick, E. P. Previc, Joseph Casanova, Jr., and E. Herbert Carlson, *J. Org. Chem.*, **21**, 1087 (1956); (b) P. L. Southwick and R. T. Crouch, *J. Am. Chem. Soc.*, **75**, 3413 (1953); (c) P. L. Southwick and L. L. Seivard, *J. Am. Chem. Soc.*, **71**, 2532 (1949).

(4) (a) P. L. Southwick and J. Casanova, Jr., *J. Am. Chem. Soc.*, **80**, 1168 (1958); (b) P. L. Southwick and S. E. Cremer, *J. Org. Chem.*, **24**, 753 (1959); (c) F. Kuffner, G. Lenneis, and H. Bauer, *Monatsh. Chem.*, **91**, 1152 (1960).

(5) W. L. Meyer and W. R. Vaughan, *J. Org. Chem.*, **22**, 1554, 1560 (1957).

(6) W. R. Vaughan and I. S. Covey, *J. Am. Chem. Soc.*, **80**, 2197 (1958).