with 0.1*N* sodium thiosulfate. The molarity was generally about 0.2. Aliquots in the kinetic runs were titrated in a similar manner.

Kinetic run with 5α,6β-dichloro-3β,20-diacetoxy-17(20)-pregnene (II). A specimen of II obtained by chromatography and melting at 140–150° was dissolved in the required amount of peracetic acid in benzene solution. The initial molarity of the peracetic acid was 0.187 and the peracid:enol acetate ratio, *r*, was 1.5. The titration data are plotted in Fig. 1. Excellent linearity is observed to over 80% conversion at 3.5 hr. The upward deviation beyond that time reflects lack of blank corrections. From the slope of the line (0.111 unit per hour) the rate constant, *k*, is calculated to be 4.1 l./mol.-hr.

Kinetic run with 3α,20-diacetoxy-17(20)-pregnen-11-one (V). A specimen of V melting at 118–125° (lit.,[7] 130.5–131.5°) was used. The initial molarity of the peracetic acid was 0.182 and *r* was 1.5. Small blank corrections were applied after 3 hr. A straight line (Fig. 1) is obtained for more than 5 hr. (72% conversion). From the slope (0.0515) the rate constant, *k*, is calculated to be 1.95 l./mol.-hr.

Kinetic run with 3α,11,20-triacetoxy-9(11),17(20)-pregnadiene (VI). A specimen of VI melting at 196–200° (lit.,[8] 200–201°) was used. The initial molarity of the peracetic acid was 0.181 and *r* was 2.5 to allow for possible reaction at both double bonds. Small blank corrections were applied throughout the run. Linearity (Fig. 1) is good through 4 hr. (77% conversion) and fair to 5.8 hr. (86% conversion). The slope (0.118) gives a rate constant, *k*, of 2.5 l./mol.-hr.

After 22 hr. total time, the steroid remaining was recovered and hydrolyzed to give 3α,17α-dihydroxypregnane-11,20-dione, m.p. 200.5–205°, in 85% yield.

Acknowledgments. We wish to thank the Physical and Inorganic Research Department for microanalyses and infrared spectra. We also thank Dr. George Krsek for the benefit of his experience in related work and Dr. Leon Mandell for many stimulating discussions.

RAHWAY, N. J.

[CONTRIBUTION FROM THE MERCK SHARP & DOHME RESEARCH LABORATORIES, DIVISION OF MERCK & CO., INC.]

Syntheses of Hormones from 5,6-Dichloro Steroids. III. Progesterone, 17α-Hydroxyprogesterone, and Reichstein's Substance S Acetate

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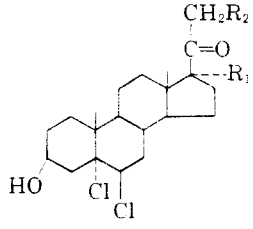
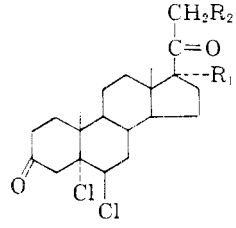
5α,6β-Dichloro-3β,17α-dihydroxypregnan-20-one has been converted to Substance S acetate in 72% yield by bromination at position 21, metathesis to the 21-acetoxy derivative, oxidation to the 3-ketone, and dechlorination with chromous chloride. Progesterone and 17α-hydroxyprogesterone have likewise been prepared by dechlorination of the appropriate ketones.

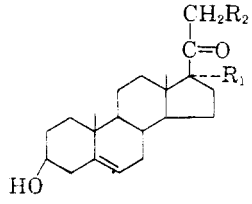
In the preceding papers of this series[1,2] the addition of chlorine to pregnenolone acetate and conversion of the dichloride to 5α, 6β-dichloro-3β, 17α-dihydroxypregnan-20-one (I) were described. In the present paper we wish to discuss the conversion of I to Reichstein's Substance S acetate, and to indicate some of the other transformations possible with various intermediate compounds.



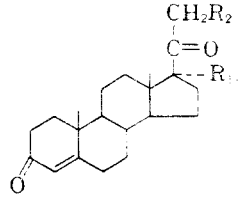
I. R_1 = OH, R_2 = H
II. R_1 = OH, R_2 = Br
III. R_1 = OH, R_2 = OAc
VI. R_1 = R_2 = H



IV. R_1 = OH, R_2 = OAc
IX. R_1 = OH, R_2 = H
VII. R_1 = R_2 = H



XI. R_1 = OH, R_2 = H
XII. R_1 = OH, R_2 = OAc



V. R_1 = OH, R_2 = OAc
VIII. R_1 = R_2 = H
X. R_1 = OH, R_2 = H

The bromination of I was carried out in hot chloroform with 1.12 moles of bromine and afforded in 92% yield crude 21-bromide II which was easily purified by recrystallization from methanol. Small amounts of the 21,21-dibromide were also isolated.

The pure 21-bromide II gave the corresponding 21-acetoxy compound III in good yield on treatment with potassium acetate in refluxing acetone. However, for practical purposes, the acetoxylation was better carried out in the presence of sodium iodide[3] and a small amount of acetic acid.[4] The

(1) F. A. Cutler, Jr., L. Mandell, D. Shew, J. F. Fisher, and J. M. Chemerda, *J. Org. Chem.*, (Paper I).

(2) F. A. Cutler, Jr., J. F. Fisher, and J. M. Chemerda, *J. Org. Chem.*, (Paper II).

(3) G. Rosenkranz, J. Pataki, St. Kaufmann, J. Berlin, and C. Djerassi, *J. Am. Chem. Soc.*, **72**, 4081 (1950).

latter procedure is efficient with crude 21-bromides, which normally contain traces of 21,21-dibromides. This was emphasized in an experimental sequence in which I was treated with 1.85 moles of bromine; the product, in spite of being largely the 21,21-dibromide, was acetoxylated in 73.7% yield to the *mono-acetoxy* compound III. Apparently the combination of acetic acid and sodium iodide serves to reduce the additional halogen rather selectively. When applied to ordinary crude II, the procedure gave a nearly quantitative yield of III. It is to be noted that in this operation, sodium iodide does not cause elimination of halogen from the 5,6-position as is the case with 5,6-dibromides.[5]

Attempts to oxidize the 3-hydroxyl of III with *N*-bromoacetamide met with failure. Normally this reagent would be expected to attack a 3β-hydroxyl of an A/B: *trans* steroid.[6] Apparently the 5,6-dichloro functionality exerts an influence at the 3-position.[7] However, oxidation with chromium trioxide was successful, giving the 3-ketone IV in 85% yield.

The removal of halogen from IV to give Substance S acetate (V) was first attempted with zinc dust in acetic acid, but only poor yields of V were obtained. In order to conserve material, the corresponding sequence leading to progesterone was studied as a model.

5α,6β - Dichloro - 3β - acetoxypregnan - 20 - one was hydrolyzed with potassium bicarbonate in aqueous methanol to the 3-alcohol VI. This in turn was oxidized with chromium trioxide to the 3-ketone VII. Treatment of VII with zinc dust under a variety of conditions gave only poor yields of progesterone (VIII); infrared spectra indicated the formation of hydroxylated products. Similar difficulties have been observed in attempts to debrominate the corresponding 5,6-dibromopregnane-3,20-dione. In this instance Julian, *et al.*[8] found that chromous chloride was a much more efficient reagent. Treatment of VII with chromous chloride was found to give excellent yields of progesterone provided that the intermediate 5-pregnene-3,20-dione[9] was isomerized with acid.

Application of the chromous chloride technique to IV gave Substance S acetate in 94% yield. The entire sequence from 3β-acetoxy-5-pregnen-20-one to Substance S acetate proceeded in about 48% yield.

It was also possible to prepare 17α-hydroxyprogesterone (X) from I by oxidation with chromium trioxide to the ketone IX and reduction by chromous chloride. In this instance, oxidative cleavage to the 17-ketone was a serious side reaction.

Reduction of I and III with chromous chloride also constitutes a convenient synthesis of 3β, 17α-dihydroxy-5-pregnen-20-one (XI) and of 21-acetoxy - 3β,17α - dihydroxy - 5 - pregnen - 20 - one (XII), respectively, as indicated in the experimental.

EXPERIMENTAL[10]

21-Bromo-5α,6β-dichloro-3β,17α-dihydroxypregnan-20-one (II). To a solution of 16.12 g. (0.04 mole) of 5α,6β-dichloro-3β,17α-dihydroxypregnan-20-one[2] (I) in 480 ml. of reagent chloroform (stabilized with about 0.75% ethanol) at 46–48° was added below the surface 116 ml. of 0.387*M* bromine in chloroform (0.0448 mole) over a period of 40 min., after the initial uptake had been established. The colorless solution was washed with 200 ml. of 10% sodium bicarbonate solution and concentrated under reduced pressure with a minimum of heat. The semicrystalline residue was slurried in 48 ml. of methanol, and after chilling the crystals were collected, washed with 16 ml. of cold methanol and dried; weight 17.7 g. (91.8%); m.p. about 185° (dec.). This material was suitable for the next step. The analytical specimen was prepared by recrystallization from methanol and decomposed at about 190°. The decomposition point of II depended greatly on rate of heating and extent of preheating. The rotation was $[\alpha]_D^{29}$ −22.8°.

Anal. Calcd. for $C_{21}H_{31}BrCl_2O_3$: C, 52.30; H, 6.48; AgX/Cmpd., 0.982. Found: C, 52.36; H, 6.76; AgX/Cmpd., 0.986.

Evaporation of the original methanol mother liquor and wash and recrystallization of the residue from acetonitrile afforded 0.37 g. of the *dibromide*, decomposing at 183–188°.

Anal. Calcd. for $C_{21}H_{30}Br_2Cl_2O_3$: AgX/Cmpd., 1.180. Found: 1.174.

21-Acetoxy-5α,6β-dichloro-3β,17α-dihydroxypregnan-20-one (III). (a) *From crude* II. Ten grams of crude 21-bromide II was dissolved in 120 ml. of acetone and 12.3 g. of anhydrous potassium acetate, 3.8 ml. of glacial acetic acid and 5.88 g. of sodium iodide were added in that order. The mixture was refluxed with agitation for 4 hr., the initial yellow iodine color fading completely during this time. Water (200 ml.) was added and the acetone was removed by distillation, finally

(4) Rosenkranz, *et al.*[3] in replacing 21-bromide by acetate *via* the 21-iodide have prepared potassium acetate by the reaction of potassium bicarbonate and acetic acid immediately before use, and found it to be superior to reagent anhydrous potassium acetate. This was confirmed in related work and the difference was traced to incomplete neutralization; adding a small amount of acetic acid to runs with reagent potassium acetate now gave equivalent results. F. A. Cutler, Jr., and W. E. Guenther, unpublished observations.

(5) P. L. Julian, E. W. Meyer, W. J. Karpel, and I. Ryden, *J. Am. Chem. Soc.*, **71**, 3574 (1949); P. L. Julian and W. J. Karpel, *J. Am. Chem. Soc.*, **72**, 362 (1950).

(6) H. Reich and T. Reichstein, *Helv. Chim. Acta*, **26**, 562 (1943).

(7) Advantage was taken of this inertness to oxidation to provide an alternate synthesis of I. 5α,6β-Dichloropregnane-3β,17α,20-triol, conveniently prepared by the action of lithium aluminum hydride on 5α,6β-dichloro-16α,17α-oxido-3β-hydroxypregnan-20-one, on oxidation with *N*-bromoacetamide or chlorine gave I. F. A. Cutler, Jr., U. S. Patent **2,811,522** (Oct. 29, 1957). This procedure has the advantage that the 20-carbonyl need not be protected as a ketal prior to reduction of the oxide by lithium aluminum hydride. P. L. Julian, E. W. Meyer, and I. Ryden, *J. Am. Chem. Soc.*, **71**, 756 (1949).

(8) P. L. Julian, W. Cole, A. Magnani, and E. W. Meyer, *J. Am. Chem. Soc.*, **67**, 1728 (1945).

(9) U. Westphal and J. Schmidt-Thomé, *Ber.*, **69**, 889 (1936).

(10) Melting points were measured with total immersion thermometers and are not corrected. Rotations were measured in chloroform at concentrations of about one gram per 100 ml.

under reduced pressure, whereupon the product separated as bulky fibers. After chilling, the product was collected, washed with water and dried; weight, 9.4 g. (98.3%); m.p. 192–195° (dec.). This material was sufficiently pure for the next step.

The analytical specimen was prepared by recrystallization from acetonitrile; m.p. 191–193.5° (dec.); $[\alpha]_D^{25}$ −19.8°. The decomposition point varied considerably with the rate of heating and extent of preheating.

Anal. Calcd. for $C_{23}H_{34}Cl_2O_5$: C, 59.86; H, 7.43; Cl, 15.37. Found: C, 59.60; H, 7.18; Cl, 15.36.

(b) *From pure II.* A mixture of 0.32 g. of II (analytical specimen), 1.0 g. of anhydrous potassium acetate, and 25 ml. of acetone was stirred and heated at the reflux temperature for 4 hr. Water (50 ml.) was added and the acetone was removed under reduced pressure. The solid was collected, washed with water and dried; weight, 0.29 g. (95%); m.p. 188–192° (dec.); infrared spectrum identical with that of pure III.

(c) *From dibromide.* Ten grams (0.0248 mole) of I dissolved in 300 ml. of chloroform was brominated in the manner described for the preparation of II using 118 ml. of 0.39*M* bromine solution (0.046 mole). The dibromide crystallized directly from the reaction mixture and after a cooling period, was collected, washed with cold chloroform and dried; weight, 9.28 g.; m.p. 190–198° (dec.). This was slurried in 100 ml. of boiling acetonitrile and collected after cooling; weight, 7.36 g.; m.p. 190–198° (dec.). Two grams of the latter material was acetoxylated in 100 ml. of acetone containing 2.08 g. of potassium acetate, 0.985 g. of sodium iodide, and 0.625 ml. of glacial acetic acid for 4 hr. at the reflux temperature. During this period the yellow iodine color rapidly formed and largely remained. The crude 21-acetoxy compound III was isolated in the usual way and recrystallized from 23 ml. of acetonitrile to give 1.21 g. (73.7% from dibromide) of III; m.p. 189–191° (dec.), undepressed on admixture with III; infrared spectrum identical with that of pure III.

In another experiment which differed from the preceding experiment in that the sodium iodide was withheld for 2 hr., a complex mixture of products resulted.

5α,6β-Dichloro-17α,21-dihydroxypregnane-3,20-dione 21-acetate (IV). Five grams of crude III was dissolved in 110 ml. of glacial acetic acid and 11 ml. of water was added to depress the freezing point. The solution was cooled to 5°. Meanwhile, a solution of chromium trioxide (2.16 g.) in water (2 ml.) and acetic acid (to a total volume of 25 ml.) was prepared. A 12.5 ml. portion of the solution was added to the steroid solution with stirring over 5 min., keeping the temperature at about 5°. Then 0.605 ml. of concentrated sulfuric acid was added over 8 min., keeping the temperature near 5°. The mixture was stirred further at 0–5° for 80 min., during which time crystallization of the product occurred. The mixture was then shaken with chloroform (250 ml.) and water (400 ml.). The aqueous phase was separated and extracted again with 50 ml. of chloroform. The combined chloroform solution was washed successively with 250 ml. of water, three 250-ml. portions of 2.5% sodium bicarbonate solution and 250 ml. of water, back-washing with chloroform as necessary. The chloroform solution was concentrated to dryness under reduced pressure, while the internal temperature was kept below 30°. The residue was triturated with a small amount of ether, transferred to a funnel, washed with minimum quantities of ether and dried. The white product weighed 4.248 g. (85%) and melted at about 190° (dec.). Such material is suitable for conversion to Substance S acetate.

Samples of this compound have been stored without serious deterioration for several months at room temperature. There is some tendency toward spontaneous loss of hydrogen chloride. For analysis the compound was recrystallized from ethyl acetate. It then decomposed at 202°; $[\alpha]_D^{25}$ −7.6°.

Anal. Calcd. for $C_{23}H_{32}Cl_2O_6$: C, 60.13; H, 7.02; Cl, 15.44. Found: C, 60.79; H, 6.77; Cl, 15.63.

Substance S acetate (V). A solution of chromous chloride was first prepared as follows[11]: Zinc dust (400 g.) was amalgamated by shaking with 400 ml. of water containing 32 g. of mercuric chloride and 20 ml. of concentrated hydrochloric acid. The aqueous phase was decanted and 800 ml. of water, 80 ml. of hydrochloric acid and 200 g. of chromic chloride were added. Carbon dioxide was bubbled through the mixture to provide agitation and prevent reoxidation by air. When the solution was blue, it was ready for use.

To a solution of 9.21 g. of IV in 650 ml. of boiling acetone was added in a slow stream 740 ml. of chromous chloride solution. The resulting mixture was then concentrated under reduced pressure until the acetone was removed. The resulting suspension was chilled, filtered, and the product washed with water until the washes were colorless and neutral. The crude product gave a negative Beilstein halogen test and showed λ_{max}^{MeOH} 241 mμ (ϵ = 13,000). To complete the isomerization of the double bond, the crude product was dissolved in 370 ml. of boiling acetone and 9 ml. of 1*N* sulfuric acid in acetone was added. The solution was boiled down to a volume of 135 ml. during 9 min. The solution was then chilled, and the crystals were collected, washed with cold acetone, and dried to constant weight *in vacuo* at room temperature; weight, 6.84 g. (88%); m.p. 235–240°; λ_{max}^{MeOH} 241 mμ (ϵ = 16,600)[12]; infrared spectrum identical with that of authentic Substance S acetate. The material gave a scarlet color in concentrated sulfuric acid.

From the acetone mother liquors there was obtained by concentration and recrystallization, an additional 0.47 g. (6%) of Substance S acetate, m.p. 237–241°, bringing the total yield to 94%.

5α,6β-Dichloro-3β-hydroxypregnan-20-one (VI). A mixture of 5 g. of 5α,6β-dichloro-3β-acetoxypregnan-20-one,[1] 3.7 g. of potassium bicarbonate, 160 ml. of methanol, and 12 ml. of water was heated at reflux for 1 hr. The resulting solution was concentrated under reduced pressure to 40 ml. and diluted with 150 ml. of water. After cooling, the crystals were collected, washed and dried. The material weighed 4.32 g. and melted at 154–157° after a transition at about 90° (hydrate?).

The analytical specimen was recrystallized from a mixture of petroleum ether, ethyl ether, and acetone, and melted at 160–160.5°.

Anal. Calcd. for $C_{21}H_{32}Cl_2O_2$: C, 65.12; H, 8.32; Cl, 18.31. Found: C, 64.85; H, 8.21; Cl, 18.30.

5α,6β-Dichloropregnane-3,20-dione (VII). The oxidation of VI was carried out by essentially the same procedure used to prepare IV. From 3 g. of VI there was obtained 2.55 g. (85%) of VII, whose melting point depended on the rate of heating. When heated in the usual way from room temperature, it decomposed at 129–131°. However, if a specimen was placed in a bath held at 140°, 40 seconds elapsed before decomposition occurred. On storage for a day at room temperature, the material turned pink and began to lose hydrogen chloride.

For analysis the material was recrystallized from acetone-ether with no significant change in melting point.

Anal. Calcd. for $C_{21}H_{30}Cl_2O_2$: C, 65.45; H, 7.85; Cl, 18.40. Found: C, 66.23; H, 7.70; Cl, 18.05.

Progesterone (VIII). (*a*) *By zinc dust.* To a solution of 1 g. of VII in 20 ml. of glacial acetic acid maintained at 40–45° was added 2.0 g. of zinc dust in small portions over 90 min. with continuous agitation. The mixture was filtered and the zinc cake was washed with 20 ml. of acetic acid. The combined filtrate and wash was diluted with 160 ml. of water and chilled. The flocculent precipitate was collected,

(11) G. Rosenkranz, O. Mancera, J. Gatica, and C. Djerassi, *J. Am. Chem. Soc.*, **72**, 4077 (1950).

(12) Reported, m.p. 239–241°; ϵ_{2410} 17,400 (methanol). B. A. Koechlin, T. H. Kritchevsky, and T. F. Gallagher, *J. Am. Chem. Soc.*, **73**, 189 (1951).

washed, and dried; weight, 0.68 g.; m.p. 137–173°; Beilstein halogen test, negative. The infrared spectrum showed peaks at 2.93 (hydroxyl), 5.89 (carbonyl), 6.03 (conjugated carbonyl), and 6.19 μ (carbon–carbon double bond), but no acetate bands. Numerous variations in the above procedure gave similar poor results.

(b) *By chromous chloride.* To a solution of 500 mg. of VII in 100 ml. of acetone at room temperature was slowly added 40 ml. of chromous chloride solution. Reduction was virtually instantaneous, as judged by color. Water (200 ml.) was added and the acetone was removed under reduced pressure. The resulting suspension of crystals was chilled and filtered, yielding 400 mg. (98%) of material giving a negative Beilstein halogen test and melting at 140–155° after softening at 115°.[13] To complete the isomerization of the double bond, 100 mg. of the material was dissolved in 2 ml. of ethanol and 6 drops of *N* sulfuric acid in ethanol was added. The solution was refluxed for 6 min., then diluted with water. The progesterone was collected, washed, and dried; yield, 90 mg.; m.p. 120.5–122°, undepressed on admixture with authentic material; infrared spectrum identical with that of authentic material.

17α-Hydroxyprogesterone (X). The oxidation of 5α,6β-dichloro-3β,17α-dihydroxypregnan-20-one (I) was carried out essentially as described for the preparation of IV. The yield of crude 5α,6β-dichloro-17α-hydroxypregnane-3,20-dione (IX) was 60–70%, and the material decomposed unsharply in the range 145–170°. Chromous chloride reduction in refluxing acetone gave a halogen-free product whose infrared spectrum showed at peak at 5.78 μ, indicating that the oxidation product had contained a considerable amount of 17-ketone due to cleavage of the side chain. Isomerization with a trace of acid followed by recrystallization from methanol gave 17α-hydroxyprogesterone, m.p. 219–222° (lit.,[14] 222–223°). The yield from I was about 30%.

3β,17α-Dihydroxy-5-pregnen-20-one (XI) was prepared in 80% yield by the reduction of 5 g. of I in 500 ml. of acetone with 400 ml. of chromous chloride solution. Recrystallized from methanol, the material melted at 262–268° (lit.,[15] 271–273°).

3β,17α,21-Trihydroxy-5-pregnen-20-one 21-acetate (XII). Reduction of 10 g. of III in 250 ml. of acetone with 500 ml. of chromous chloride solution by heating for 5 min. at the reflux temperature afforded 8.0 g. (94%) of crude XII. This was recrystallized twice from acetonitrile, the first time involving a charcoal treatment, then from methanol, and finally again from acetonitrile to give 3.96 g. of XII, m.p. 209–213° (lit.,[16] 211–213°). Acetylation of XII with acetic anhydride in pyridine gave the 3,21-diacetate, m.p. 196–199° (lit.,[16] 195°).

Acknowledgment. We wish to thank the staff of the Physical and Inorganic Research Department for microanalyses and for spectral determinations.

RAHWAY, N. J.

(13) 5-Pregnene-3,20-dione is reported[9] to melt at 158–160°.

(14) J. v. Euw and T. Reichstein, *Helv. Chim. Acta*, **24**, 879 (1941).

(15) P. Hegner and T. Reichstein, *Helv. Chim. Acta*, **24**, 828 (1941).

(16) J. Heer and K. Miescher, *Helv. Chim. Acta*, **34**, 359 (1951).

[CONTRIBUTION FROM THE DEPARTMENT OF BIOLOGICAL SCIENCES STANFORD RESEARCH INSTITUTE]

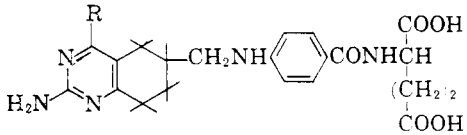
Potential Anticancer Agents.[1] XXIV. Tetrahydroquinazoline Analogs of Tetrahydrofolic Acid. II.

JOSEPH DEGRAW, LEON GOODMAN, RUTH KOEHLER, AND B. R. BAKER

Received June 2, 1957

A variety of 6-substituted 5,6,7,8-tetrahydroquinazolines were prepared in which the substituents at 2 and 4 were mercaptohydroxy, dihydroxy, dichloro, diamino, and bis(benzylamino). The use of the dichloro-, diamino-, and bis(benzylamino)-5,6,7,8-tetrahydroquinazolines in synthetic schemes designed to prepare intermediates for the synthesis of 5,8-dideaza-5,6,7,8-tetrahydroaminopterin, is described.

In a preceding work of this series[2] the synthesis of 5,8-dideaza-5,6,7,8-tetrahydrofolic acid (I) was described. The key compound in the synthesis of I was 2-amino-5,6,7,8-tetrahydro-4-hydroxy-6-quinazolinecarboxylic acid (VIII). In the course of that work a number of other substituted 5,6,7,8-tetrahydroquinazolines were prepared and, subsequent to that work, many more such compounds have been synthesized as part of an attempted synthesis of 5,8-dideaza-5,6,7,8-tetrahydroaminopterin (II), the 4-amino analog of I. Although the work has not achieved the synthesis of II, the interesting chemistry involved prompts a description of the observations.



I. R = OH
II. R = NH_2

Condensation of dimethyl 4-oxo-1,3-cyclohexanedicarboxylate (III)[2] with thiourea proceeded readily in the presence of sodium methoxide to give a good yield of methyl 5,6,7,8-tetrahydro-4-hydroxy-2-mercapto-6-quinazolinecarboxylate (V). In contrast with the condensation of III with

(1) This work was carried out under the auspices of the Cancer Chemotherapy National Service Center, National Cancer Institute, Contract No. SA-43-ph-1892. For the preceding paper of this series, *cf.* E. J. Reist, P. A. Hart, L. Goodman, and B. R. Baker, *J. Am. Chem. Soc.*, **81**, 5176 (1959).

(2) R. Koehler, L. Goodman, J. DeGraw, and B. R. Baker, *J. Am. Chem. Soc.*, **80**, 5779 (1958).