changing 1-methyl-2-quinolone into 2-chloroquinoline. Recrystallization from acetone combined with decolorizing carbon treatments was used in purification of VI.

Anal. Calcd. for $C_9H_4Cl_3N$: N, 6.03. Found: N, 5.90.

2,6,8-Trichloro-5-nitroquinoline (A).—2,6,8-Trichloroquinoline (22 g.) dissolved in sulfuric acid (sp. gr. 1.84, 105 ml.) was added dropwise, with stirring, to nitric acid (sp. gr. 1.42, 52 ml.) maintained at 0°. After keeping for an additional hour at 0–5°, temperature of system was allowed to increase to 25° and was finally gradually increased by application of heat to 70°. Twenty minutes later the solution, at 70°, was poured with stirring into cracked ice–water mixture (1000 ml.). The solid which separated was collected by filtration, washed with water, and purified by applying decolorizing carbon treatments along with alternate crystallizations from acetone and 95% ethanol; yield 21.5 g.; m.p. 151.5–153°.

Anal. Calcd. for $C_9H_3Cl_3N_2O_2$: Cl, 38.34; N, 10.10. Found: Cl, 38.44; N, 9.99.

(B).—6,8-Dichloro-1-methyl-5-nitro-2-quinolone (1.4 g.) was treated with phosphorus oxychloride–phosphorus pentachloride mixture under essentially the same conditions as those employed by de Arce, Greene and Capps[3] for converting 8-bromo-1,6-dimethyl-5-nitro-2-quinolone into 8-bromo-2-chloro-6-methyl-5-nitroquinoline. The temperature of oil-bath was maintained at 140–150° for 1.5 hours, and purification was by a combination of decolorizing carbon treatments and recrystallizations from 95% ethanol.

6,8-Dichloro-1-methyl-5-nitro-2-quinolone.—6,8-Dichloro-5-nitroquinoline was converted into the corresponding dimethyl sulfate addition-product and oxidized with 30% hydrogen peroxide under conditions similar to those previously reported by Capps[7] for changing 6-methyl-8-nitroquinoline into 1,6-dimethyl-8-nitro-2-quinolone. The period of heating with dimethyl sulfate at 125–130° was for three hours and the oxidation was carried out at 55–65°. 6,8-Dichloro-1-methyl-5-nitro-2-quinolone crystallized from methanol as needles; m.p. 144–145°.

Anal. Calcd. for $C_{10}H_6Cl_2N_2O_3$: N, 10.26. Found: N, 10.07.

6,8-Dichloro-2-hydroxyquinoline.—2,6,8-Trichloroquinoline (5 g.) was mixed with 20 ml. of 3:1 by volume sulfuric acid (sp. gr. 1.84)–water solution, and the resulting system was placed in an oil-bath maintained at 170–210° for 3.5 hours before pouring system with stirring into 200 ml. of cold water. The crude 6,8-dichloro-2-hydroxyquinoline was collected by filtration, washed with water and recrystallized from 95% ethanol (400 ml.); yield almost theoretical; m.p. 255–256°.

Anal. Calcd. for $C_9H_5Cl_2NO$: N, 6.57. Found: N, 6.50.

6,8-Dichloro-2-hydroxy-5-nitroquinoline (A).—Nitric acid (sp. gr. 1.42, 5 ml.) was added slowly with shaking to a solution of 6,8-dichloro-2-hydroxyquinoline (2.0 g.) in sulfuric acid (sp. gr. 1.84, 5 ml.) prior to gradually increasing temperature to 55° and maintaining at 55° for five minutes. After spontaneously cooling to room temperature, the solution obtained was poured with stirring into 250 ml. of cold water. The resulting solid was collected by filtration, washed with water and recrystallized from 95% ethanol (400 ml.); 2.0 g. yield; m.p. 255–257°. It was later shown that 2-ethoxyethanol (Cellosolve) is a good recrystallizing solvent to employ in the purification of this compound.

Anal. Calcd. for $C_9H_4Cl_2N_2O_3$: N, 10.81. Found: N, 10.60.

(B).—6,8-Dichloro-2-hydroxy-5-nitroquinoline was obtained in nearly theoretical yield from 2,6,8-trichloro-5-nitroquinoline by the application of the same conditions as employed by de Arce, Greene and Capps[3] for hydrolyzing 8-bromo-2-chloro-6-methyl-5-nitroquinoline.

5-Amino-2,6,8-trichloroquinoline and 5-Amino-6,8-dichloro-2-hydroxyquinoline.—2,6,8-Trichloro-5-nitroquinoline and 6,8-dichloro-2-hydroxyquinoline were reduced in reagent grade acetone and absolute ethanol, respectively, with hydrogen in presence of Raney nickel catalyst at 50°; m.p. of 5-amino-2,6,8-trichloroquinoline, 207–208°, and of 5-amino-6,8-dichloro-2-hydroxyquinoline, 259–260.5° dec.

Anal. Calcd. for $C_9H_5Cl_3N_2$: N, 11.32. Found: N, 11.24. Calcd. for $C_9H_5Cl_2N_2O$: N, 12.23. Found: N, 12.12.

(7) J. D. Capps, THIS JOURNAL, **69**, 176 (1947).

5-Amino-6,8-dichloroquinoline.—6,8-Dichloro-5-nitroquinoline (13 g.) was reduced with tin and hydrochloric acid under the usual conditions and the resulting amine was extracted with boiling acetone from the solid obtained after making the reaction mixture basic with sodium hydroxide. The acetone extract was treated with decolorizing carbon prior to diluting with water at boiling point of solution and slowly cooling to cause precipitation of amine as needles; yield 7.4 g.; m.p. 181–182°.

Anal. Calcd. for $C_9H_6Cl_2N_2$: N, 13.15. Found: N, 13.29.

5-Acetamido-6,8-dichloroquinoline, 5-Acetamido-2,6,8-trichloroquinoline and 5-Acetamido-6,8-dichloro-2-hydroxyquinoline.—5-Amino-6,8-dichloroquinoline, 5-amino-2,6,8-trichloroquinoline and 5-amino-6,8-dichloro-2-hydroxyquinoline were acetylated under conditions similar to those employed by de Arce, Greene and Capps[3] for acetylation of 5-amino-8-bromo-6-methylquinoline to give the respective acetamido derivatives melting at 247–248.5°, 299–300° and above 310°. 5-Acetamido-6,8-dichloroquinoline was recrystallized from 95% ethanol; 5-acetamido-2,6,8-trichloroquinoline was recrystallized from 50% by volume acetone–ethanol; and impurities were extracted from 5-acetamido-6,8-dichloro-2-hydroxyquinoline with boiling ethanol, its solubility in ethanol being too low for recrystallization.

Anal. Calcd. for $C_{11}H_8Cl_2N_2O$: N, 10.98. Found: N, 10.82. Calcd. for $C_{11}H_7Cl_3N_2O$: N, 9.67. Found: N, 9.72. Calcd. for $C_{11}H_8Cl_2N_2O_2$: N, 10.33. Found: N, 10.40.

5-Benzamido-2,6,8-trichloroquinoline.—5-Amino-2,6,8-trichloroquinoline was benzoylated according to instructions recorded by de Arce, Greene and Capps[3] for benzoylation of 5-amino-8-bromo-6-methylquinoline; m.p. 259–260° from 95% ethanol.

Anal. Calcd. for $C_{16}H_9Cl_3N_2O$: N, 7.96. Found: N, 8.11.

6,8-Dichloro-5-quinolinearsonic Acid and 2,6,8-Trichloro-5-quinolinearsonic Acid.—5-Amino-6,8-dichloroquinoline (8.9 g.) and 5-amino-2,6,8-trichloroquinoline (8.0 g.) were diazotized and converted into arsonic acids according to procedure reported by Capps and Hamilton[8] for changing certain 2-chloroaminoquinolines into 2-chloroquinolinearsonic acids. 6,8-Dichloro-5-quinolinearsonic acid and 2,6,8-trichloro-5-quinolinearsonic acid resulted in yields of 30 and 8.9%, respectively, melting at 292–293° and above 310°.

Anal. Calcd. for $C_9H_6Cl_2NAsO_3$: As, 23.96. Found: As, 23.07. Calcd. for $C_9H_5Cl_3NAsO_3$: As, 21.02. Found: As, 20.82.

(8) J. D. Capps and C. S. Hamilton, *ibid.*, **60**, 2105 (1938).

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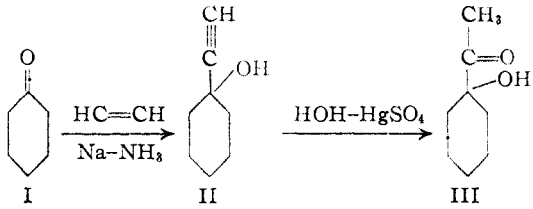
1-Acetylcyclohexanol

BY GARDNER W. STACY AND CHARLES A. HAINLEY

The recently reported scheme of Billimoria and Maclagen[1] for the introduction of the cortisone side chain into simple alicyclic ring systems prompts the early publication of our work in this same direction. The method described by these investigators involves, as an intermediate, 1-acetylcyclohexanol (III) which was obtained from 1-hydroxycyclohexanecarboxylic acid by reaction with methyllithium.

The synthetic procedure for the introduction of the side chain which was conceived by us is quite similar to that of Billimoria and Maclagen[1] and like their method involves 1-acetylcyclohexanol (III) as a key intermediate; however, the synthesis from cyclohexanone by our procedure involves only two reactions. In this way we have obtained 1-acetylcyclohexanol from 1-ethynylcyclohexanol (II) in

(1) J. D. Billimoria and N. F. Maclagen, *Nature*, **167**, 81 (1951).



yields of about 70%. This hydration was accomplished by using, with some modification, the procedure of Locquin and Wouseng.[2] The 1-acetylcyclohexanol obtained failed to give a Tollens test or a fuchsin–aldehyde test but readily gave a positive iodoform test. The yellow precipitate was isolated, and its identity with an authentic sample of iodoform was demonstrated by a mixed melting point determination. The substance (III) was further characterized by conversion to an oxime and a semicarbazone.

Experimental[3]

1-Ethynylcyclohexanol (II).—The procedure of Saunders[4] was employed with some modification. As this author points out, lower yields are obtained if all the liquid ammonia is allowed to evaporate to leave a residual solid. In our hands this factor was observed to be quite critical. The rate of evaporation of ammonia varies with the ventilating system. Whereas a 20-hour period was recommended for evaporation of ammonia in the original procedure, in our case it was found that not more than four to five hours should be allowed for this operation. Otherwise yields dropped to 30% or below.

The procedure was further modified in that the crude product was washed with saturated sodium bisulfite solution, as well as with sodium chloride to remove any unreacted cyclohexanone that might possibly be present. Yields of about 50% were obtained.

1-Acetylcyclohexanol (III).—To a solution of 27 ml. of concentrated sulfuric acid and 135 ml. of water, to which had been added 4.1 g. of mercuric oxide, was added 40.0 g. (0.322 mole) of 1-ethynylcyclohexanol in small portions over a period of 15 minutes. A white oil, which floated on the surface of the mixture, formed rapidly. By means of a separatory funnel the aqueous layer was separated from the oil and was placed in a three-necked flask equipped with stirrer, condenser and dropping funnel. While the contents of the flask were being heated to the boiling point, the temperature of the white oil was maintained between 20–25° by cooling in an ice-bath (in one case where this was not done a vigorous, exothermic reaction took place causing the organic material to char). While the mixture was heated under reflux, the white oil was added in small portions from a dropping funnel at such a rate so as not to cause the reaction to become too vigorous (about one-half hour required). It was important that only a fraction of the total amount of material be placed in the dropping funnel at any one time. The main portion of the oil was retained in the beaker and cooled in an ice-bath from time to time so as to maintain the temperature of the material within the limits described above. If these precautions were not observed (*i.e.*, if the entire amount of white oil was placed in the dropping funnel at one time), a violent reaction was likely to proceed up the stem of the dropping funnel causing the oil to char and making further addition difficult. After addition was complete, the mixture was heated under reflux for five minutes and then allowed to cool to room temperature. The reaction mixture was then extracted with 150 ml. of ether followed by two 50-ml. portions. The combined extracts were washed with 50 ml. of saturated sodium chloride solution and dried over anhydrous sodium sulfate. The ether was removed, and the black residue distilled, b.p. 90–93° (15 mm.), $n^{25}D$ 1.4673; yield 31.4 g. (69%).

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.66; H, 9.63.

Oxime of 1-Acetylcyclohexanol.—The oxime was prepared and recrystallized three times from hot water for analysis, m.p. 107–108°.

Anal. Calcd. for $C_8H_{15}NO_2$: C, 61.12; H, 9.62; N, 8.91. Found: C, 60.87; H, 9.49; N, 8.97.

Semicarbazone of 1-Acetylcyclohexanol.—This derivative was prepared in the customary manner and recrystallized four times to give fine white needles. This substance melted with decomposition, and the decomposition point varied with the rate at which the bath was heated. If the bath was heated at a rate of about 3° per minute, the decomposition point was 208–209°; on the other hand, if the temperature of the bath was raised more rapidly (about 8° per minute), the decomposition point was 217–218°.[5]

Anal. Calcd. for $C_9H_{17}N_3O_2$: C, 54.25; H, 8.60; N, 21.09. Found: C, 54.43; H, 8.58; N, 21.23.

(2) R. Locquin and S. Wouseng, *Compt. rend.*, **176**, 516 (1923).

(3) Melting points are corrected. The microanalyses were performed by the Clark Microanalytical Laboratory, Urbana, Illinois.

(4) J. H. Saunders in *Org. Syntheses*, **29**, 47 (1949).

(5) Billimoria and Maclagen (ref. 1) reported a melting point of 221°.

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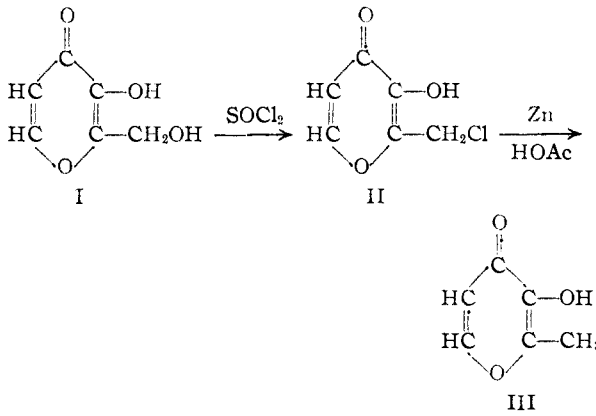
The Structure of the Pyrone from Hydroxystreptomycin

BY FRANK H. STODOLA

In previous papers,[1,2] was reported the isolation of a maltol-like compound from the reaction of hydroxystreptomycin with alkali. From a consideration of its chemical and physical properties this compound was tentatively assigned the structure I. We have now established the correctness of this formulation by conversion of the new pyrone, by way of the chloro derivative (II) into maltol (III).



The procedure employed was essentially that described by Yabuta[3] for converting kojic acid (IV) into the chloro compound (V) and allomaltol (VI).

The formation of the chloro compound from kojic acid proceeds without difficulty, yields as high as 78% having been reported by Kipnis.[4] The yield of the new chloro derivative (II), however, was considerably less due to the formation of tarry by-products. Compound II is, moreover, readily decomposed by hot water to which the chloro compound V appears to be insensitive. This instability may be explained on the basis of vinylogy since

(1) Benedict, Stodola, Shotwell, Borud and Lindenfelser, *Science*, **112**, 77 (1950).

(2) Stodola, Shotwell, Borud, Benedict and Riley, THIS JOURNAL, **73**, 2290 (1951).

(3) Yabuta, *J. Chem. Soc.*, 578 (1924).

(4) Kipnis, THIS JOURNAL, **70**, 4264 (1948).