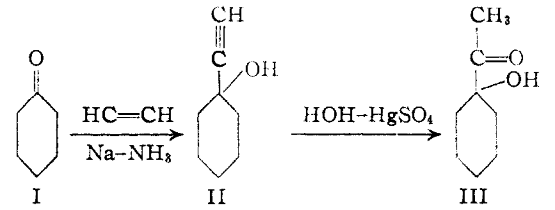


yields of about 70%. This hydration was accomplished by using, with some modification, the procedure of Locquin and Wouseng.[2] The 1-acetylcyclohexanol obtained failed to give a Tollens test or a fuchsin–aldehyde test but readily gave a positive iodoform test. The yellow precipitate was isolated, and 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).

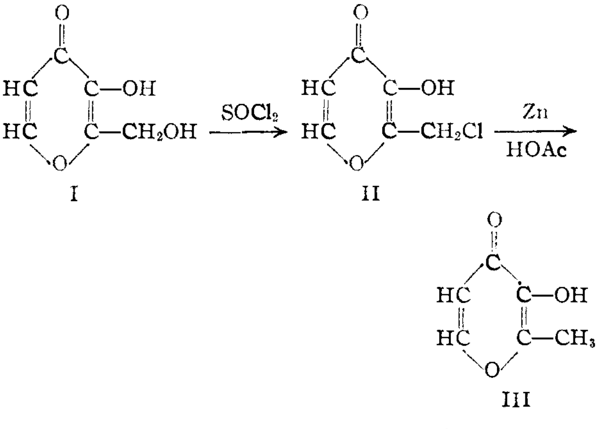
[5] Billimoria and Maclagen (ref. 1) reported a melting point of 221°.

THE FULMER CHEMICAL LABORATORY
THE STATE COLLEGE OF WASHINGTON
PULLMAN, WASHINGTON
RECEIVED JULY 30, 1951

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 byproducts. 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

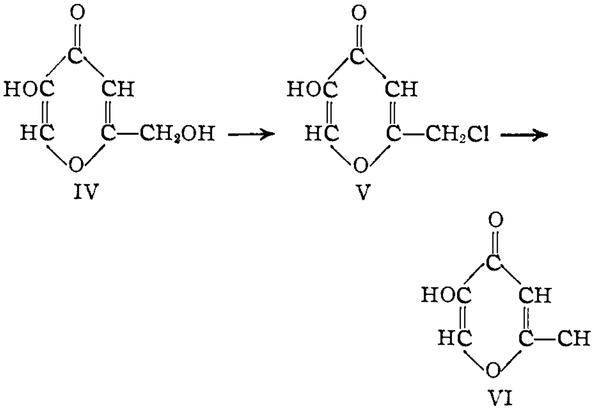
---

[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).



IV V VI

the grouping $HO-[\overset{|}{C}=\overset{|}{C}]-CH_2Cl$ might be expected to show some of the behavior of $HOCH_2Cl$.

Experimental

2-Chloromethyl-3-hydroxy-1,4-pyrone (II).—The pyrone from hydroxystreptomycin (289 mg.) was refluxed with 1.5 ml. of dry chloroform and 0.5 ml. of purified thionyl chloride. After 10 minutes, 0.4 ml. of thionyl chloride and 1 ml. of chloroform were added and the refluxing continued for 30 minutes more. The dark brown solution was concentrated *in vacuo* to almost black crystals. Crystallization from benzene gave 140 mg. of dark brown crystals melting at 120–140°. Sublimation followed by crystallization from benzene yielded 40 mg. of pure chloro compound in the form of white needles.

Anal. Calcd. for $C_6H_5O_3Cl$: C, 44.9; H, 3.14; Cl, 21.6. Found: C, 44.6; H, 3.49; Cl, 21.9.

The chloro compound started to sinter and darken at 137° and melted at 145–146° to a red melt. It gave a violet color with ferric chloride and was decomposed by hot water with the liberation of hydrochloric acid.

Reduction of the Chloro Compound.—The chloro compound (58 mg.) was dissolved in 1.5 ml. of acetic acid and 350 mg. of zinc dust added. The reaction mixture was worked with a glass rod for 10 minutes. After removal of the excess zinc, the acetic acid solution was treated with hydrogen sulfide, diluted with water and the zinc sulfide removed by filtration. The filtrate was neutralized and then made slightly acid with hydrochloric acid. Extraction with ether gave 25 mg. of crystals which were purified by sublimation and crystallization from benzene. The 20 mg. of colorless product analyzed correctly for maltol.

Anal. Calcd. for $C_6H_6O_3$: C, 57.1; H, 4.80. Found: C, 57.6; H, 4.88.

The material had the characteristic odor of maltol and gave a violet color with ferric chloride. It melted at 147.5–148.5° (uncor.) and showed no depression in melting point with carefully purified maltol (m.p. 148.5–149.5°).

Further confirmation was obtained by conversion to the benzoate. For this purpose 5.5 mg. of the product was benzoylated with 6 mg. of benzoyl chloride in pyridine. Crystallization from dilute alcohol and then acetone–petroleum ether gave 6.8 mg. of maltol benzoate (m.p. 113–114°, cor.) which showed no depression in melting point on admixture with an authentic sample (m.p. 114–115°, cor.).

FERMENTATION DIVISION
NORTHERN REGIONAL RESEARCH LABORATORY[5]
PEORIA, ILLINOIS

RECEIVED AUGUST 6, 1951

---

[5] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

A Modified Method for the Meerwein-Ponndorf-Verley Reduction

BY W. L. TRUETT AND W. N. MOULTON

Although it is generally assumed in the reduction of carbonyl compounds by aluminum isopropoxide that the acetone formed must be removed in order to obtain good yields,[1] several α-haloketones[2,3] and one β-aminoketone[4] have been successfully reduced without removal of acetone.

TABLE I

Compound reduced	Product	Yield,[a] %	n_D or m.p.,[b] °C.	Method
Benzophenone	Benzhydrol	96	64–66	A_1
		98	63–65	A_2
		98	60–62	A_3
Benzosuberone[c]	Benzosuberol[d]	94	102.5–104.5	A_1
		99	90–95	A_2
		99	98–100	A_3
dl-Camphor	*dl*-Isoborneol *dl*-Borneol	92[e]	167–172	A_1
Cinnamylideneacetone[f]	1-Phenylhexa-1,3-diene-5-ol[g]	76[h]	60–62	A_1
Cyclopentanone	Cyclopentanol	60	1.4387[i]	B
β-Piperidylpropiophenone[j]	1-Phenyl-3-piperidylpropanol-1-hydrochloride[k,l]	40[h]	134–135.5	A_1
Benzaldehyde	Benzyl alcohol	85	1.5321[i]	B
Phenyl-2-methoxy-1-naphthyl ketone[m]	Phenyl-2-methoxy-1-naphthylcarbinol	0[n]	80–90	A_1
		95	98–100	C
Benzoin	*meso*-Hydrobenzoin	94	131–134	A_1
α-Benzylaminodesoxybenzoin[o]	1,2-Diphenyl-2-benzylaminoethanol hydrochloride[o,l]	72[h]	225–229	A_1
Benzalacetophenone	1,3-Diphenyl-2-propene-1-ol[p]	76[h]	57–59	A_1
Pinacolone	Pinacolyl alcohol	36	1.3980[i]	B

[a] Yield refers to the crude product unless otherwise noted. [b] Melting points (uncorrected) are listed for solid products, refractive indices (at 25°) for liquid products. [c] This compound was prepared by the method of Pl. A. Plattner [*Helv. Chim. Acta*, **27**, 801 (1944)]. [d] This compound was reported by G. Baddeley and J. Chadwick [*J. Chem. Soc.*, 368 (1951)], m.p. 100–101°. [e] The yield stated represents a mixture of isomers. Isoborneol was isolated from the mixture by preparation of its *p*-nitrobenzoate in 30% yield, m.p. 125.5–126.5°. [f] This compound was prepared by the method of J. T. Plati, W. H. Strain and S. L. Warren [THIS JOURNAL, 65, 1273 (1943)]. [g] This compound has been reported by A. K. Macbeth and J. A. Mills [*J. Chem. Soc.*, 2646 (1949)], m.p. 65–66°. [h] Yield stated is that of the purified compound crystallized from the appropriate solvent. [i] The low value of the refractive index is believed due to the difficulties inherent in the purification of small quantities of liquids. The material gave a negative 2,4 DNPH test by the method reported in R. L. Shriner and R. C. Fuson ["Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N.Y., 1948, p. 171]. [j] This compound was prepared by the method of F. F. Blicke ["Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N.Y., 1942, p. 329]. [k] This compound has been reported by C. Mannich and D. Lammerling [*Ber.*, 55, 3510 (1922)], m.p. 138°. [l] The compound was isolated by the addition of ethereal hydrogen chloride to the dried ether extract of the crude product. [m] The ketone was prepared by the method of F. E. Ray and W. A. Moomaw [THIS JOURNAL, 55, 3833 (1933)]; Dr. C. F. Koelsch furnished us with a generous sample. The carbinol was also reported by the above investigators, m.p. 98°. [n] Although the melting point of the crude product prepared by method A_1 suggests the presence of the carbinol, crystallization of the material yielded only unreduced ketone, m.p. 123–123.5°, 80% recovery. [o] The ketone was prepared by the method of R. E. Lutz, J. A. Freek and R. S. Murphy [THIS JOURNAL, 70, 2015 (1948)]. The carbinol was also reported by these investigators, m.p. 228–229°. [p] This compound was reported by H. Meerwein and R. Schmidt [*Ann.*, 444, 221 (1925)], m.p. 57–58°.

---

(1) A. L. Wilds, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 178.

(2) (a) S. Winstein, *et al.*, *J. Org. Chem.*, **11**, 150 (1946); (b) S. Winstein, *et al.*, THIS JOURNAL, **68**, 1831 (1946).

(3) R. E. Lutz, J. F. Codington and N. H. Leake, *ibid.*, **69**, 1260 (1947).

(4) R. E. Lutz, R. H. Jordan and W. L. Truett, *ibid.*, **72**, 4085 (1950).