from benzene or from a benzene–petroleum ether solution yielded platelets whose "melting" point depended on the rate of heating as described above. *Anal.* Calcd. for 3-hydroxymethylindole: C, 73.4; H, 6.16. Found: C, 73.2; H, 6.03. The infrared spectrum showed the N–H bond stretching peak at 2.97 $m\mu$, and a shoulder at about 3.05 $m\mu$ ascribed to hydrogen-bonded hydroxyl.

The reduction was also carried out in an aqueous dioxane solution, and the same product was obtained.

Sodium Borohydride Reduction of 2-Pyrrolealdehyde.—A solution of 2.0 g. of sodium borohydride in 10 ml. of water was added over a period of ten minutes to a stirred solution of 1.8 g. of 2-pyrrolealdehyde in 30 ml. of water. The temperature rose to 42°. After one hour, the solution was saturated with potassium carbonate and extracted with ether. The ether solution was dried and evaporated, and the residue was distilled at 81–83° at 2 mm. The distillate was a colorless, moderately viscous oil; yield 1.3 g. (71%) *Anal.* Calcd. for 2-hydroxymethylpyrrole: C, 61.8; H, 7.27. Found: C, 61.9; H, 7.14; $n^{20}{}_{\rm D}$ 1.5425; $d^{20}{}_{4}$ 1.130; $(\rm R)_{\rm D}$ calcd. 27.3, found 27.1; mol. wt. calcd. 97, found 104, 106 by cryoscopy in water. It was noted that the aqueous solution became slightly turbid during the measurements. By analogy with the reported behavior of 3-hydroxymethylindole,[3] probably self-condensation was occurring. The infrared spectrum showed the N–H and bonded O–H bands as described above.

Lithium Aluminum Hydride Reduction of 2-Pyrrolealdehyde.—A slurry of 0.8 g. of lithium aluminum hydride in ether was added dropwise to a stirred solution of 2.0 g. of 2-pyrrolealdehyde in 50 ml. of dry ether. The mixture was stirred for 15 minutes after the addition was completed, and the excess hydride and the organic salt were decomposed with a slight excess of water. The ether solution was filtered, dried and evaporated. Distillation of the residue gave 1.2 g. (59%) of 2-hydroxymethylpyrrole.

Acknowledgment.—The authors are indebted to Miss C. M. Brown and Mrs. Harriette Huff for the analytical determinations, and to Dr. H. J. Eding for the infrared spectra.

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The Rosenmund Reduction of Trichloroacetyl Chloride

BY J. W. SELLERS AND W. E. BISSINGER

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It has been claimed that trichloroacetyl chloride is a product of the oxidation of tetrachloroethylene in the presence of light, chlorine or peroxides.[1] The Rosenmund reduction of trichloroacetyl chloride would be of interest as a method of preparing chloral. When the acyl halide was reduced under modified Rosenmund conditions dichloroacetyl chloride was produced in 50–60% yields. No chloral was found. If the reduction were carried out under ordinary Rosenmund conditions[2] (in xylene at 110° using 2% palladium–barium sulfate catalyst, and a quinoline-S regulator) wherein 0.25 millimole of hydrogen chloride was evolved per minute, the acid evolution abruptly stopped when 2 moles of hydrogen chloride had appeared per mole of acid chloride (6 hr.). The product did not contain any material having a boiling point below 125°. When the reaction was stopped after the evolution of 1 mole of hydrogen chloride per mole of acid chloride, the product was a complex mixture of high-boiling substances. Attempts to obtain the reduction in refluxing *n*-heptane produced no acid.

Experimental[3]

Rosenmund Reduction of Trichloroacetyl Chloride.—A suspension of 40 g. (0.22 mole) of trichloroacetyl chloride,[4] 4 g. of 2% palladium–barium sulfate catalyst, 0.4 ml. of quinoline-S regulator and 190 ml. of Insectisol (a highly refined petroleum fraction which was refluxed over sodium, distilled, and the fraction, b.p. 190–220°, collected) was heated to 140°. Hydrogen was passed through the stirred mixture at such a rate that a millimole of hydrogen chloride per minute was collected in the aqueous exit gas scrubber. After 0.22 mole of HCl had been titrated (5 hr.) the mixture was cooled, filtered, and distilled. The fraction, 15.5 g. (50%), b.p. 104–106° (729 mm.),[5] was collected.

Anal. Calcd. for C_2HOCl_3: mol. wt., 147.4; Cl, 72.17. Found: mol. wt. (titration of hydrolysis products in 0.1 *N* NaOH), 146; Cl, 71.0.

The preparation of the dichloroacetanilide in benzene at room temperature[6] gave colored products difficult to purify. When prepared in acetone[7] at −5 to −10° using a 10% excess of aniline (mole ratio of acid chloride: aniline, 1:2.2) and recrystallized from 95% ethanol, the anilide, m.p. 117.5–118.5°, was obtained in 72% yield calculated on the acid chloride.

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[1] F. Kirkbride, U. S. Patent 2,321,823, June 15, 1943; E. Hart and M. Matheson, U. S. Patent 2,472,946, June 14, 1949.

[2] E. Hershberg and J. Cason, *Org. Syntheses*, **21**, 84 (1941).

[3] All melting points uncorrected.

[4] H. Brown, THIS JOURNAL, **60**, 1325 (1938).

[5] E. Gustus and P. Stevens, *ibid.*, **55**, 374 (1933).

[6] E. Votocek and J. Burda, *Ber.*, **48**, 1002 (1915).

[7] P. McKie, *J. Chem. Soc.*, **123**, 2213 (1923).

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The Preparation of Chalcones from Hydroxy and Methoxy Aldehydes and Ketones[1]

BY HERBERT E. SMITH AND MARK C. PAULSON

RECEIVED NOVEMBER 13, 1953

Four new methoxylated chalcones,[2] of possible interest as model substances for the investigation of the structure of lignin, have been prepared from hydroxy and methoxy aldehydes and ketones. The crude products were either semisolids or oils which were purified by repeated recrystallization. The recovery of significant amounts of starting materials from each preparation was not unexpected, since condensations of this nature are reversible and the yields of pure products were relatively low. The physical properties, derivatives and analyses of the chalcones are given in Table I.

Rapid cooling of the alcoholic solution of 2′-hydroxy-3,3′,4-trimethoxychalcone produced an intimate mixture of two crystalline varieties which proved to be polymorphic forms which were separable by fractional recrystallization. Controlled cooling of the clarified solution to 50–55° during recrystallization of this chalcone produced only the crystalline prismatic variety. The isolation of minute quantities of 3′,4′,8-trimethoxyflavanone and veratric acid from the reaction mixture indicated that acid isomerization of the 2′-hydroxychalcone[3] and oxidation of the aldehyde

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[1] This note is based on a portion of a thesis submitted by Herbert E. Smith in partial fulfillment of the requirements for the degree of Master of Science at Bradley University.

[2] The number system used for the substituted chalcones is that of *Chemical Abstracts*.

[3] St. von Kostanecki and W. Szabranski, *Ber.*, **37**, 2634 (1904)

TABLE I

Compound	Color	M.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Methoxyl, % Calcd.	Methoxyl, % Found	2,4-Dinitrophenylhydrazone M.p., °C.	2,4-Dinitrophenylhydrazone Empirical formula	2,4-Dinitrophenylhydrazone Nitrogen, % Calcd.	2,4-Dinitrophenylhydrazone Nitrogen, % Found
2′,4-Dihydroxy-3,3′-dimethoxychalcone ($C_{17}H_{16}O_5$)	Orange	128–129	67.89	67.8	5.37	5.36	20.7	20.7	241–242	$C_{23}H_{20}O_8N_4$	11.7	12.3
2′-Hydroxy-3,3′,4-trimethoxychalcone[a,b] ($C_{18}H_{18}O_5$)	Red	128–129.5	68.77	68.9	5.77	5.79	29.6	29.8	190–191 d	$C_{24}H_{22}O_8N_4$	11.33	11.44
3′4′8-Trimethoxyflavanone ($C_{18}H_{18}O_6$)	Colorless	142–143	68.77	68.7	5.77	5.7	29.6	29.7	....	....	...	...
2,2′3,3′-Tetramethoxychalcone[c] ($C_{19}H_{20}O_5$)	Yellow	71–74	69.5	69.6	6.14	6.12	37.8	37.8	177–179	$C_{25}H_{24}O_8N_4$	11.9	10.4

[a] Acetyl derivative described in Experimental. [b] Yield 26.7%. [c] Yield 21.8%.

occurred to a limited extent under the reaction conditions.

Attempts to prepare 4-hydroxy-2′,3,3′-trimethoxy- and 4-acetoxy-2′,3,3′-trimethoxychalcones by both acid- and alkali-catalyzed condensation of 2,3-dimethoxyacetophenone with vanillin and vanillinmonoacetate, respectively, were unsuccessful.

Experimental[4]

General Procedure.—To a stirred solution of equimolar quantities of the aldehyde and ketone in the minimum amount of absolute alcohol was added portionwise an aqueous alkali hydroxide solution. The flask was stoppered and allowed to stand for 24 hours. The mixture was diluted with ice-water, and acidified with hydrochloric acid to congo red. If the resulting precipitate was crystalline or a semi-solid, it was dried and crystallized repeatedly from alcohol or an alcohol–water mixture with the aid of decolorizing charcoal.

Isolation of 3′,4′,8-Trimethoxyflavanone.—The mother liquor from the crystallization of 2′-hydroxy-3,3′,4-trimethoxychalcone (0.3-mole run) was concentrated to about 126 ml., and cooled overnight. The pale orange crystals were recrystallized from alcohol with the aid of decolorizing charcoal to yield a colorless crystalline product. Qualitative tests for unsaturation and the hydroxyl group were negative. This material gave the characteristic yellow color reaction for flavanones with an aqueous solution of sodium hydroxide, and with hot aqueous solution of sodium bicarbonate or sodium carbonate. The colorless crystalline product was identified by analysis as 3′,4′,8-trimethoxyflavanone; yield 0.9 g.

2′-Acetoxy-3,3′,4-trimethoxychalcone.—Direct acetylation of an anhydrous pyridine solution of 2′-hydroxy-3,3′,4-trimethoxychalcone (0.0016 mole) with freshly distilled acetyl chloride (1.5 ml.) yielded the acetoxy derivative of this chalcone. The reaction mixture was worked up in the usual manner, and the crude product was twice recrystallized from an ethanol-water mixture (50%) with the aid of decolorizing charcoal, yielding a yellow crystalline product, m.p. 107–109°, yield 0.15 g. (26.7%).

Anal. Calcd. for $C_{20}H_{20}O_6$: acetyl, 12.0. Found: acetyl, 11.7.

Preparation of 2′,4-Dihydroxy-3,3′-dimethoxychalcone.[5]—The general procedure failed to give the desired chalcone, and the following technique was used: Alcoholic solutions containing equimolar quantities (0.066 mole) of vanillin and 2-hydroxy-3-methoxyacetophenone, respectively, were combined, stirred and cooled to −5°. With continued stirring, 152 ml. of potassium hydroxide solution (60%) was added portionwise, and the salts that formed were redissolved by adding an alcohol–water mixture, and heating on the steam-bath for 3 hours. After standing at room temperature for 15 days (with occasional shaking) excluded from air, the reaction product was diluted with ice-water, and acidified with hydrochloric acid to congo red. The acid solution was decanted, and the gummy mass was washed three times with water. An ether solution of the gummy material was extracted with water until neutral, then dried, and the solvent was removed by distillation and evaporation. The ether-free, dried, semi-crystalline material was steam distilled, and the product was twice recrystallized from an alcohol–water mixture with the aid of decolorizing charcoal; yield 2.0 g. (10.2%).

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[4] Melting points are uncorrected.

[5] Modification of the cold condensation technique described by T. A. Geissman and R. O. Clinton, THIS JOURNAL, **68**, 697 (1946).

The Isomerization of D-Glucose by a Strong Base Resin

BY JOHN C. SOWDEN

RECEIVED APRIL 14, 1954

In a recent communication,[1] Rebenfeld and Pacsu described the isomerization of D-glucose by the strongly basic anion-exchange resin Amberlite IRA-400.[2] They analyzed the isomerized mixture by a combination of the alkaline hypoiodite and Somogyi methods, neither of which are specific for individual sugars, and recorded the results as "% glucose" and "% fructose." Finally, they concluded that "—it appears that the presently accepted ene–diol mechanism for the Lobry du Bruyn transformation does not hold in this case, as evidenced by the absence of mannose in the glucose–fructose interconversion."

It is apparent that the above data alone cannot validly be used to conclude that D-mannose is not formed in the isomerization reaction. Moreover, since D-mannose is a very minor constituent[3,4] of the alkaline isomerization products from D-glucose, failure to detect it on a paper chromatogram of the reaction mixture would constitute at best a tenuous basis for assuming its absence.

Since the conclusion reached by Rebenfeld and Pacsu concerning the reaction mechanism would be, if correct, of considerable importance, it was desirable to repeat their isomerization experiment in order to determine the presence or absence of D-mannose in the products. In the present work it was observed that D-mannose *is* formed from D-glucose in the presence of Amberlite IRA-400-(OH) to approximately the same extent as from D-glucose in the presence of dilute aqueous sodium hydroxide. The interpretation placed on their work by Rebenfeld and Pacsu therefore must be considered invalid.

Experimental

Ten grams (dry weight, chloride form) of Amberlite IRA-400 was cycled several times through the chloride and hydroxide forms. To the conditioned, moist resin in the hydroxide form was added a solution of 2.0 g. of D-glucose

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[1] L. Rebenfeld and E. Pacsu, THIS JOURNAL, **75**, 4370 (1953).

[2] A product of Rohm and Haas Co., Philadelphia, Pa.

[3] M. L. Wolfrom and W. L. Lewis, THIS JOURNAL, **50**, 837 (1928); R. D. Greene and W. L. Lewis, *ibid.*, **50**, 2813 (1928).

[4] J. C. Sowden and R. Schaffer, *ibid.*, **74**, 499 (1952).