Summary

4,4-Dimethylpentene-1 has been prepared from allyl bromide and *tert*-butylmagnesium chloride, and purified through its dibromide. Addition of hydrogen bromide takes place contrary to Markownikoff's rule, giving 1-bromo-4,4-dimethylpentane exclusively. The latter has been converted to 4,4-dimethylpentanol-1 through the Grignard reaction. 4,4-Dimethylpentene-1 does not add dry hydrogen iodide at 0–5°; it reacts with acetic acid in the presence of sulfuric acid yielding the acetate of 4,4-dimethylpentanol-2 and a mixture of olefins.

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Hydrogenolysis of Sugars

BY WALTER H. ZARTMAN AND HOMER ADKINS

Since certain types of glycols undergo cleavage at carbon to oxygen or carbon to carbon linkages when submitted to the action of hydrogen over a suitable catalyst, it seemed of interest to ascertain the facts with regard to the behavior of the sugars under these conditions. The experimental results of this study of the hydrogenolysis of the more common sugars may, perhaps, be most concisely and clearly presented by first giving a description of the experimental procedure and observations with respect to sucrose.

A rapid reaction ensued when 171 g. (0.5 mole) of sucrose in 175 ml. of dry ethanol with 20 g. of copper–chromium oxide at 250° was subjected to the action of hydrogen under a pressure of about 300 atmospheres.[1] During the course of two or three hours about 4.7 moles of hydrogen was absorbed, whereupon the reaction apparently stopped. After centrifuging out the catalyst the perfectly colorless reaction mixture was fractionated through an electrically heated Widmer column, having a spiral 20 cm. in length. Alcohol and water were distilled at atmospheric pressure. Fractionation of the remainder at 7 mm. resulted in a distillation curve similar to that marked "A" in Fig. 1. There was apparently a large amount of a compound boiling at about 80° (7 mm.), a very small amount at about 138° (7 mm.), a larger fraction at about 175° (7 mm.), with 22 g. of higher boiling material.

The fraction collected at atmospheric pressure was obviously largely composed of the ethanol originally used as the solvent. Analysis of it by the method of Wright showed that it contained about 4 g. of methanol.[2]

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[1] The catalyst and apparatus has been described by Connor, Folkers and Adkins, THIS JOURNAL, **54**, 1140 (1932), and Adkins, *Ind. Eng. Chem.*, *Anal. Ed.*, **4**, 342 (1932); see also Connor and Adkins, THIS JOURNAL, **54**, 4678 (1932), on hydrogenolysis of glycols.

[2] Wright, *Ind. Eng. Chem.*, **19**, 750 (1927).

Calculations based upon the amount and density of the fraction showed that it contained about 24 g. of water and 13 g. of ethanol, resulting from the hydrogenolysis of the sucrose. The fraction boiling at 78–83° (7 mm.) was readily identified as propanediol-1,2. The higher boiling fractions were too small in amount for their purification and identification from a single hydrogenolysis. However, the careful fractionation at 1 mm. of the material boiling above 83° (7 mm.) from several reaction mixtures gave three fractions: I, b. p. 118–125°; II, b. p. 142–144°; and III, b. p. 214–215°. The analysis of I showed its formula to be $C_6H_{12}O_3$, the analysis of II showed $C_6H_{14}O_3$, while III was found to be $C_6H_{14}O_4$. The molecular refractions of these compounds as well as other data showed I to be a dihydroxy ether, II a trihydric alcohol, and III a tetrahydric alcohol. The tentative structural formulas suggested for these compounds are, respectively

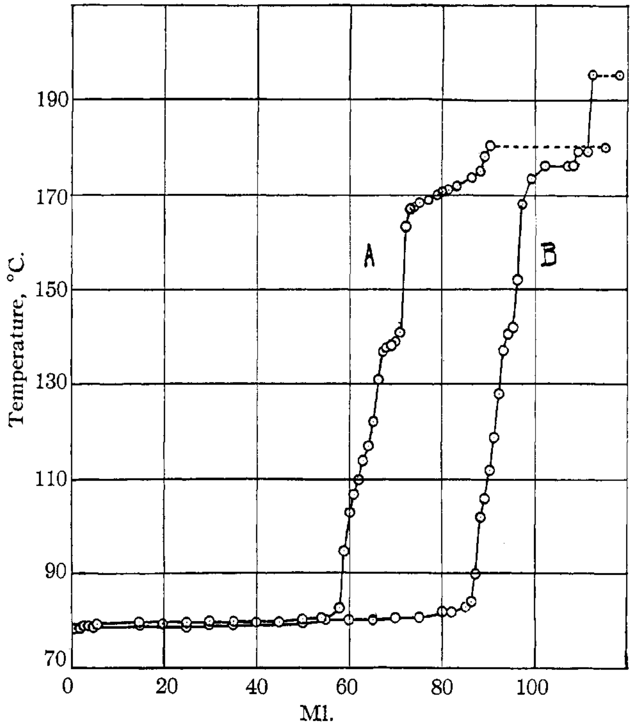
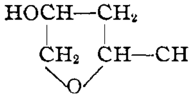


Fig. 1.—Distillation curves of products boiling above 78° (7 mm.) from lactose (A) and mannitol (B).



2-(4-Hydroxytetrahydrofuryl)-methylcarbinol

I

$CH_2OHCHOHCH_2CH_2CHOHCH_3$

Hexanetriol-1,2,5

II

$CH_2OHCHOHCH_2CH_2CHOHCH_2OH$

Hexanetetrol-1,2,5,6

III

TABLE I

HYDROGENOLYSIS OF SUGARS

Moles sugar and H_2			CH_3OH, g.	C_2H_5OH, g.	H_2O, g.	C_3H_6-$(OH)_2$, g.	$C_6H_{10}O$-$(OH)_2$, g.	C_6H_{11}-$(OH)_3$, g.	C_6H_{10}-$(OH)_4$, g.	Residue, g.
1.0	Glucose	4.9	6	10	25	91	6	13	..	17
1.0	Sorbitol	4.2	6	14	18	93	6	9	12	Trace
1.0	Mannitol	4.2	4	15	27	90	4	17	5	5
0.5	Sucrose	4.7	4	13	24	54	11	16	11	22
0.5	Lactose	4.6	4	19	23	54	7	20	9	23
0.5	Maltose	4.6	5	14	32	59	5	17	..	32
0.7	α-Methyl-*d*-glucoside	3.1	6	6	22	20	6	12	10	3
0.3	Pentacetylglucose	3.9	1	..	19	6	12	3	..	5
1.0	Gluconic lactone	4.8	2	15	29	16	15	(6 g. $C_2H_4(OH)_2$)		55

The assignment of positions to the various hydroxyl groups is based principally upon the following considerations. First, no two hydroxyls may be in the 1,3 or β position with respect to each other, for hydroxyl groups in such positions are very unstable over copper–chromium oxide at 250° under high pressures of hydrogen. This statement is based upon observations on the behavior of many 1,3 glycols in this Laboratory by Folkers, Connor, Wojcik, Sprague and others. The presence of a CH_3-CHOH group in I and II and the absence of such a group in III was shown by the iodoform test. These facts in the case of compounds I and III can apparently only be reconciled by the formulas given above. Compound II might have the 1,4,5 rather than the 1,2,5 structure but the latter is preferable on account of its closer relationship to I and III, and because the hydroxyls in the 3 and 4 positions should be eliminated first on hydrogenolysis since each of them has two hydroxyls in the β position with respect to it.

There is given in Table I a summary of the data on the absorption of hydrogen, and the weight of the various products obtained from glucose, sorbitol, mannitol, sucrose, lactose, maltose, α-methyl-*d*-glucoside, pentacetylglucose, and gluconic lactone under the conditions described above for sucrose.[3,4] The data given on the true sugars and for gluconic lactone are the averages of two or more duplicate experiments, those on the other four compounds represent single experiments. In no case was there any material variation on duplicate experiments. For the purpose of tabulation the material boiling over the range 78–83° (7 mm.) is listed as $C_3H_8O_2$, 130–145° (7 mm.) as $C_6H_{12}O_3$, and 165–180° (7 mm.) as $C_6H_{14}O_3$. The material listed as "residue" contained no appreciable amounts of unchanged sugar but was largely $C_6H_{14}O_4$. The yields of the higher boiling products are materially increased by interrupting the hydrogenolysis after the absorption of 2 or 3 moles of hydrogen.

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(3) The materials used in this investigation were commercially available or were prepared by standard methods.

(4) The hydrogenation of mannitol, glucose, sucrose and similar compounds over a metal of the platinum or iron group is claimed: I. G. Farbenind., German patent 541,326 (1927); *Chem. Abst.*, **26**, 1939 (1932); French Patent 662,874 (1928), *Chem. Abst.*, **24**, 378 (1930).

There is a close similarity in the behavior toward hydrogenolysis of glucose, sorbitol, mannitol, sucrose, maltose and lactose. The disaccharides took up 4.6 to 4.7 moles of hydrogen per 0.5 mole of sugar but there was a considerable "residue" after distillation of the products. The equivalent amount of glucose (1.0 mole) took up 4.9 moles of hydrogen with a less "residue" than the disaccharides. The hexahydric alcohols took up 4.2 moles of hydrogen with very small residues. Since 1 mole of hydrogen had already been taken up by these alcohols in the course of their preparation from the hexoses, it would thus appear that one mole of the simple sugar or the equivalent 0.5 mole of the disaccharide would take up about 5.3 moles of hydrogen. The statement that reaction apparently stopped after the absorption of about 5 moles of hydrogen per mole of monosaccharide should not be taken to mean that the glycols obtained would not undergo further hydrogenolysis at 250° under 300 atmospheres of hydrogen over copper–chromium oxide. In fact, some of the "residues" were converted into the lower boiling products previously isolated when again subjected to the action of hydrogen. The elimination of hydroxyl groups from the glycols therefore occurs but the reaction is very slow as compared to the hydrogenolysis of the sugars themselves. It appears that a rapid hydrogenolysis of the sugars occurs with the absorption of a little over 5 moles of hydrogen per mole of monosaccharide and that the rate of the reaction then changes very markedly.

There is one very marked difference between the three disaccharides and glucose (or the hexahydric alcohols) which is brought out by a comparison of the distillation curves for the products from lactose and mannitol as given in Fig. 1. The yield of propanediol-1,2 from the latter group is more than 60% greater than that from the former. This difference in yields of the glycol shows that the first step in the hydrogenolysis of the disaccharides is not the cleavage of the disaccharide to monosaccharides or the corresponding hexahydric alcohols.

The yields of propanediol-1,2 from α-methyl-*d*-glucoside and pentacetylglucose were quite low as compared with that from the parent sugar.

PROPERTIES AND ANALYSES OF PRODUCTS

No.	Compound	B. p., °C. (1 mm.)	d_{25}^{25}	n_D^{25}	MR_D Calcd.	MR_D Found
1	2-(4-Hydroxytetrahydrofuryl)-methylcarbinol	118–125	1.1452	1.4752	32.40	32.48
2	Hexanetriol-1,2,5	142–144	1.1075	1.4732	34.32	33.97
3	Hexanetetrol-1,2,5,6	214–215	....	....	...	...

		Analyses, %					
		Carbon			Hydrogen		
No.	Formula	Calcd.	Found		Calcd.	Found	
1	$C_6H_{12}O_3$	54.50	54.89	54.83	9.10	9.29	9.29
2	$C_6H_{14}O_3$	53.70	53.19	53.32	10.44	10.41	10.43
3	$C_6H_{14}O_4$	48.00	48.20	48.00	9.33	9.39	9.34

Gluconic lactone was the only one of the derivatives of the sugars submitted to hydrogenolysis which did not react smoothly. A large amount of non-volatile tarry material was obtained. Noteworthy was the formation of ethylene glycol from this lactone as well as a relatively high yield of the 2-(4-hydroxytetrahydrofuryl)-methylcarbinol. The formation of this latter compound is not surprising since gluconic lactone contains the same ring structure as does the tetrahydrofuran derivative represented in Formula I.

Summary

Glucose, sorbitol, mannitol, sucrose, lactose, maltose, α-methyl-*d*-glucoside, pentacetylglucose and gluconic lactone in ethanol solution have been submitted to the action of hydrogen under 300 atmospheres at 250° in the presence of a copper–chromium oxide catalyst. All of the compounds under these conditions undergo a rapid hydrogenolysis to methanol, ethanol, propanediol-1,2 and three additional hydroxy compounds to which the following tentative formulas have been assigned, 2-(4-hydroxytetrahydrofuryl)-methylcarbinol, hexanetriol and hexanetetrol. No attempt is made to formulate the series of reactions involved in the formation of these products because, in our opinion, there is no conclusive evidence on the basis of which a choice may be made between several alternatives. However, the formation of each of the products is understandable in consideration of the behavior toward hydrogenolysis of simpler glycols, aldehydes and ketones which are being studied in this Laboratory.

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The Action of Carbon Monoxide on Iron and Cobalt Complexes of Cysteine

BY MAXWELL P. SCHUBERT

I. Introduction.—In continuation of studies of the iron and cobalt complexes of thiol acids, the reaction of carbon monoxide with these compounds has been taken up. Cremer[1] was the first to observe that solutions of ferrous and cobaltous complexes of cysteine absorb carbon monoxide and from a study of the maximum amount absorbed and the proportion of metal to cysteine under which this takes place, concluded that there must exist in solution the complexes $Fe(cysteine)_2(CO)_2$ and $Co(cysteine)_2(CO)$. The concern of the present paper is the actual isolation of the complexes which occur in solutions of ferrous and of cobaltous biscysteinate after they have absorbed carbon monoxide.

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[1] W. Cremer, *Biochem. Z.*, **206**, 228 (1929).